NATIONAL BUREAU OF STANDARDS REPORT

6297

Preliminary Report
on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and Their Compounds With Oxygen, Hydrogen, Fluorine, and Chlorine
(Revised)

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January 1, 1959

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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First Technical Summary Report
to the Advanced Research Projects Agency
on the Thermodynamic Properties
of Light-Element Compounds

Reference: ARPA Order No. 20-59

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

PREFACE

The National Bureau of Standards is undertaking an experimental and theoretical investigation of the thermodynamic properties of light-element compounds. This research program presently comprises the chemical elements lithium, beryllium, magnesium, and aluminum, free and in combination with hydrogen, oxygen, fluorine, and/or chlorine. It has as its objective the securing of the basic information which is necessary to determine, with an accuracy of one per cent where possible, the energies and equilibrium proportions of these substances in the solid, liquid, and gaseous states in the temperature range from 0° to 6000°K and the pressure range from 0 to 100 atmospheres.

The first year's program at NBS involves nine groups--namely, those in fluorine calorimetry, low-temperature calorimetry, high-temperature calorimetry, statistical thermodynamics, high-temperature high-pressure phenomena, spectra, chemical preparation, thermochemistry, and thermodynamics of refractory substances. This program is a part of a broader program at the National Bureau of Standards on properties of materials at high temperatures now required in many technical and scientific fields.

Chas W Beckett
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Thermodynamics Section
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ABSTRACT

The National Bureau of Standards has begun a more extensive experimental and theoretical investigation of the thermodynamic properties of the elements Al, Be, Mg, and Li, and their compounds with H, O, F, and Cl in the temperature range 0° - 6000°K and the pressure range 0 - 100 atmospheres. The results of a critical survey of the literature on the existing data are presented in detail. The values that have been previously reported are discussed critically in most cases, recommended or estimated "best" values are tabulated (together with estimates of uncertainty in many cases), and references are given. The properties and number of substances for which values are tabulated are: Heat capacity and entropy at 298.15°K, 28; heat content as a function of temperature above 298.15°K, 18; molecular constants, 16 diatomic and 19 polyatomic molecules; vapor pressure and heat of vaporization, the four metals and, briefly, the oxides of Al and Be; heat of fusion of Al_2O_3; standard heats of formation and/or dissociation energies, approximately 70. Tables of ideal-gas thermal functions for these 16 diatomic molecules have been computed and are presented; tables for additional ideal gases are to be computed at a later date. The preparation of pure samples suitable for accurate physical measurements also is discussed at some length. In general, the existing thermodynamic data on these compounds are found to be fairly complete from 0° to 1000°K, considerably less complete from 1000° to 2000°K, and almost totally lacking for condensed phases above 2000°K. Accurate values of the ideal-gas thermodynamic properties are available for the monatomic and a few of the diatomic gases. At present the configurations, force constants, and dissociation energies of most of the polyatomic gases are highly uncertain. Apart from a few triatomic molecules no molecular data exist.

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CHAPTER I

PROGRAM OBJECTIVES, AND SUMMARY OF THE CURRENT STATUS OF THE THERMODYNAMIC DATA

C. W. Beckett and T. B. Douglas

As part of its comprehensive program on the properties of materials over wide ranges of temperature and pressure, the National Bureau of Standards is conducting an experimental and theoretical investigation of the thermodynamic properties of the oxides, hydroxides, hydrides, fluorides, chlorides, and elemental species of lithium, beryllium, magnesium, and aluminum. This investigation has as its goal the securing of the basic information which is necessary to determine the energies and equilibrium proportions of these substances in the solid, liquid, and gaseous states at different pressures up to about 100 atmospheres and at all temperatures of interest up to 6000°K. Other substances or other properties that acquire importance may be included as the program progresses.

The program is composed of the following phases:

(a) A comprehensive, up-to-date, and critical survey of the literature to locate the pertinent data already existing.

(b) A calculation of tables of values of heat, free energy, and "equilibrium constant" of formation, and of free-energy function, heat-content function, entropy, heat content, and heat capacity, of the above substances as applicable, at temperatures in intervals of 100° or less up to 6000°K. These values will be interconsistent and will be those believed to be the best available at the time.

(c) An experimental program yielding accurate thermal data on some of these substances. Wherever the need is great enough, the measurements will include heat capacities over the temperature range of approximately 14° to 1800°K and heats of reaction.

(d) An investigation yielding as far as possible the equilibrium constants and heats of formation of the gaseous species of these substances which are stable at high temperatures. This phase of the work will, where possible, include theoretical estimations of the fundamental molecular constants of the species likely to exist. Experimental studies to measure the same also will be made, producing high temperatures by hot flames or rapid compression and measuring the abundance of gaseous species spectroscopically.

(e) Revisions and extensions of the tables of thermodynamic functions as more reliable data become available.

The results to date of what is labeled above as "phase (a)" of the program constitute the body of this report. Each of the next five chapters covers one type of thermodynamic property, discusses the most important values reported, and where possible states the reasons for selecting for each substance the "best" value given in an accompanying table.

It has been the aim to arrive at a set of those interconsistent basic data which are necessary and sufficient to compute the tables of thermodynamic properties described above as "phase (b)." The participating staff have examined systematically the available literature of abstracts, reports, compilations, and original papers too recent to be referenced elsewhere, as well as all other important original papers so far as time has permitted. The difficulties of arriving at reliable "best" values, and more particularly, limits of uncertainty, are well known. It should be emphasized that this report should be regarded as preliminary and incomplete for the following reasons.

1. On some subjects now being actively investigated in different laboratories, important publications are continuously appearing, and undoubtedly some of those already issued have escaped attention.

2. In some cases competing values have been cited or referenced in this report, but time has thus far been insufficient for comparing them critically. This is particularly true of heats of formation, which in some cases can be derived independently from calorimetry, equilibrium data, spectroscopic observations, theoretical calculations, or some other source.

3. Sometimes the data appear so sketchy or lacking in precision that it has seemed unwise to recommend any "best" value without further study or experimental investigation.

4. Ideal-gas functions, calculated at the Bureau, are tabulated for only a few substances at the end of this report. In succeeding months these tables will be augmented to include, so far as possible, all those specified above under "phase (b)" of the program.

Chapter VII deals with methods of chemical preparation and purification of the classes of substances involved in this program, a necessary preliminary to accurate measurement of their thermodynamic and other properties. Some substances present special problems in securing samples whose purity is high enough to be consistent with the accuracy of the measurements. Also, the thermodynamic properties of some solids have no exact meaning unless the crystal form and size are standardized and established.

One of the important purposes of the present literature survey and analysis has been to indicate what substances and properties most urgently need investigation in future phases of this program, in order to fill the gaps in existing knowledge.

The current status of the thermodynamic data on these substances may be conveniently summarized with reference to different temperature ranges. From 0° to 1000°K the data are in general rather complete and fairly good for the substances stable in this temperature range. Thus heats of formation and heat contents have been measured for most of the stable solids and liquids, with a few exceptions such as the halides of beryllium. But the chemical instability of the hydrides and all the hydroxides except LiOH, as well as the low volatility of most of the other substances, has precluded accurate measurement of their vapor pressures and heats of vaporization, as well as spectroscopic observation of their vapors, in this temperature range.

Between 1000° and 2000°K such techniques as those of temperature measurement and particularly the availability of suitable container materials are less favorable, but still not so formidable but that a considerable number of thermodynamic measurements on some of these substances has been made. In this region of higher temperatures, however, there are numerous cases of complete lack of data, or else measurements exist whose reliability is doubtful partly because only one investigator has reported values. The existing heat-content data, for example, span this temperature range for some refractory substances (as MgO), but for most of the substances under discussion which melt between 1000° and 2000°K (such as Be and Li_2O) the data do not extend up to the melting point and the heat of fusion has never been measured directly. Some gas-condensed-state equilibrium data exist for all the stable substances, and these results give some measure of the effective heats of vaporization, but in no case except the free metals is the composition of the gas phase known with sufficient accuracy. A vigorous attack on this problem in recent years by means of physical measurements of the vapors by such techniques as optical and mass spectrometry and molecular beams has indeed provided some semi-quantitative information, particularly on the halides, but the results have usually been incomplete or difficult to interpret unambiguously.

Above 2000°K there are virtually no data on condensed states. Existing tables are essentially empirical extrapolations (from lower temperatures) which are uncertain in most cases by about 10% in the heat capacity. The properties of the gaseous species are quite accurately known for the monatomic and for a few of the diatomic species. There are several deficiencies in the latter, however. For one thing, we have very little molecular data in some cases. In many cases, the dissociation energies are uncertain by some 10%. Many of the excited states of the molecules are unobserved and are omitted in the conventional treatment. Higher-order correction terms for the ground states are treated in an approximate way which is fairly satisfactory in view of the relatively large uncertainties in other data such as the dissociation energies.

Numerous polyatomic species have been observed at low pressures (approximately 10^{-6} atm.) by vaporization of refractory solids and of liquids into mass spectrometers, and for a few of these molecules other data are available such as the electron-diffraction and infrared spectra. But the number of polyatomic molecules for which the configuration and other molecular constants for the ground state have been established is quite small relative to the number of possibilities that may arise from the eight elements under consideration. The excited states of these molecules are virtually unknown and are neglected in the statistical thermodynamic calculations.

As the result of this lack of data, the extrapolation of vapor-state properties from 2000° to 6000°K is quite uncertain in many cases. Moreover, the treatments for these different types of molecules and different phases are not consistent. Hence, relatively large errors are likely to occur in the treatment of vapor-liquid or vapor-solid equilibria at temperatures above the current experimental range. Moreover, as the pressure increases along the saturation line--from 10^{-6} atm. at 2000° to 1 atm. at 4000° and perhaps to 1000 or 2000 atm. at 6000°K--large clusters in the vapor state may be postulated. For these species, which are not molecules in the ordinary sense used by chemists, we have neither the experimental nor the theoretical techniques required for their investigation. Hence the extrapolation of temperature by a factor of two or three and an extrapolation of vapor pressure (and related properties) to 100 atm.--and perhaps beyond to 1000 atm., where a critical region may occur--is still in the realm of speculation.

CHAPTER II

HEAT CAPACITY, ENTROPY, AND HEAT CONTENT FUNCTION AT 298.15°K

G. T. Furukawa and Jeanette M. Henning

In the low-temperature heat-capacity phase of this literature survey the results of original measurements below about 400°K were compiled. The data compiled above 298.15°K were primarily for the purposes of joining smoothly the lower temperature data with those of higher temperature. Because of the short time allocated for this preliminary compilation, no attempt was made to obtain smoothed heat capacities at equally spaced integral temperatures from 0° to 298.15°K from which the various thermal functions could be evaluated. Instead, for this preliminary summary report, the original values of the heat capacity published by the various investigators were plotted on a scale sufficiently large for comparison, and the results from the best single experimental work in which the desired thermal properties had been evaluated were adopted. These selected values of heat capacity and entropy were compared with compilations given in the Bureau of Mines Bulletin 477 [K. K. Kelley, Contributions to the Data on Theoretical Metallurgy. XI. Entropies of Inorganic Substances. Revision (1948) of Data and Methods of Calculation, 1950] and National Bureau of Standards Circular 500 [F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe; Selected Values of Chemical Thermodynamic Properties, February, 1952]. In those instances where the investigator did not evaluate the entropy from the heat-capacity data, the adopted value was that taken from the above compilations.

Generally, when the experimental data are reliable, the separate re-evaluations in the above compilations do not show significant variations from the thermal functions computed by the original investigator from his measurements. On those substances on which the available data were not of high accuracy, there are only a few cases in which the entropies at 298.15°K given in the two compilations differ significantly. The tabulated values of the heat capacity, on the other hand, have been found to differ considerably in many of these cases.

Some of the substances of interest have been investigated for the first time since the publication of the above-mentioned compilations. Because low-temperature heat-capacity measuring techniques have been highly refined, the results of new investigations in which thermal properties were derived have been accepted with good confidence.

In this compilation, the substances of interest have been separated into four groups--those containing aluminum, beryllium, magnesium, and lithium. Substances containing two of these metallic elements have been placed in the more basic group. All selected values of the heat capacity and entropy are given for the condensed phase in defined calories (4.1840 abs j = 1 defined calorie) per degree per gram formula mass at 1 atm pressure and 298.15°K. Enthalpy functions are given whenever available. All temperatures are in degrees Kelvin unless otherwise indicated.

The substances of each group are discussed separately after listing the low-temperature heat-capacity measurements in chronological order, with reference and the temperature range of each investigation. The chemical and physical nature of the material, wherever known is given along with the source of the adopted values. These values are compared with those given in earlier compilations. Tables of the adopted thermal properties follow the discussion of each elemental group. References given in the tables are those from which the values of thermal properties have been adopted. Estimates of the accuracy are given wherever possible. A list of references arranged in alphabetical order is given at the end of each section.

A. Aluminum and Its Compounds

1. Aluminum, Al

Low-temperature measurements of the heat capacity of aluminum have been published by Nernst [12] (32° to 88°), Nernst and Schwers [13] (19° to 79°), Griffiths and Griffiths [3,4] (158° to 371°), Maier and Anderson [10] (54° to 296°), Kok and Keesom [9] (1° to 20°), and Giauque and Meads [2] (15° to 302°). The values of heat capacity, entropy, and heat-content function were adopted from those obtained by Giauque and Meads [2] on single-crystal aluminum of 99.944 per cent purity. The values given in Kelley [6], Stull and Sinke [18], and NBS C-500 [15] are the same as those adopted.

2. Aluminum Hydride, $(AlH_3)_x$

No low-temperature heat-capacity data have been found on this substance.

3. Aluminum Oxide, Al_2O_3

Parks and Kelley [14] (91° to 291°); Simon and Swain [17] (30° to 280°); Kerr, Johnston, and Hallett [7] (20° to 295°); Furukawa, Douglas, McCoskey, and Ginnings [1] (13° to 1170°); and Morrison and Patterson [11] (78° to 270°) have published results of low-temperature measurements on sapphire (α - Al_2O_3). The measurements by Parks and Kelley were on natural sapphire, while the others were on synthetic materials. The values of heat capacity, entropy, and heat-content function were adopted from those tabulated by Furukawa, Douglas, McCoskey, and Ginnings [1]. Kelley [6] gives for the heat capacity and entropy 18.90 cal/deg mole and 12.5 e.u., respectively, while NBS C-500 [15] gives 18.88 cal/deg mole and 12.186 e.u., respectively, which are the same as those adopted in this compilation.

4. Aluminum Oxide Monohydrate, $Al_2O_3 \cdot H_2O$ (Böhmite?)

Shomate and Cook [16] (52° to 296°) determined the heat capacity of a sample prepared by heating the trihydrate, $Al_2O_3 \cdot 3H_2O$, at 220°C for three days. They found the sample to contain 100.12 per cent of the theoretical Al_2O_3 and, from X-ray examinations, to be similar in structure to bayerite (β - $Al_2O_3 \cdot 3H_2O$). Their published values of heat capacity and entropy have been adopted. Kelley [6] and NBS C-500 [15] give the same values for these properties.

5. Aluminum Oxide Trihydrate, $Al_2O_3 \cdot 3H_2O$ (Gibbsite)

Shomate and Cook [16] (52° to 297°) measured the heat capacity of a sample prepared by dissolving aluminum wire in potassium hydroxide. They found the material to have 100.41 per cent of the theoretical Al_2O_3 and, from X-ray examinations, to have the structure of gibbsite (α-$Al_2O_3 \cdot 3H_2O$). Their published values of heat capacity and entropy have been adopted. Kelley [6] and NBS C-500 [15] give the same values.

6. Aluminum Fluoride, AlF_3

Heat-capacity measurements have been reported by King [8] (53° to 296°) on a sample prepared by vacuum sublimation and analyzed to have 99.97 per cent of the theoretical aluminum. Their values of the heat capacity and entropy have been adopted. Kelley [6] does not give values of these properties for this substance. NBS C-500 [15] lists a considerably higher value of entropy calculated from heat and free energy of formation.

7. Aluminum Chloride, $AlCl_3$

No low-temperature heat-capacity data have been found on this substance. NBS C-500 [15] lists 21.3 and 40 cal/deg mole for heat capacity and entropy, respectively. Kelley [5[gives an equation which yields 21.6 ± 0.4 cal/deg mole for the heat capacity. The values given in NBS C-500 [15] were tentatively adopted.

8. Aluminum Oxyfluoride, AlOF

No low-temperature heat-capacity data were found on this substance.

9. Aluminum Oxychloride, AlOCl

No low-temperature heat-capacity data were found on this substance.

Heat Capacity, Entropy, and Heat Content Function of Aluminum and Its Compounds at 298.15°K

Chemical Formula	Gram Formula Mass	C°_p cal/deg mole	S° cal/deg mole	$\frac{H_{298.15^\circ K} - H_{0^\circ K}}{298.15}$ cal/deg mole	References
Al	26.98	5.82 ± 0.02	6.77 ± 0.02	3.67 ± 0.01	2
$(AlH_3)_x$	(30.004)x	----	----	----	---
Al_2O_3 α	101.96	18.88 ± 0.02	12.18 ± 0.02	8.031 + 0.010	1
$Al_2O_3 \cdot H_2O$	119.976	31.4 ± 0.1	23.2 ± 0.2	----	16
$Al_2O_3 \cdot 3H_2O$	156.008	44.5 ± 0.2	33.5 ± 0.2	----	16
AlF_3	83.98	17.95 ± 0.05	15.9 ± 0.1	----	8
$AlCl_3$	133.351	21.3 ± 0.4	40.	----	15
AlOF	61.98	----	----	----	---
AlOCl	78.437	----	----	----	---

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B. Beryllium and Its Compounds

1. Beryllium, Be

Measurements of the low-temperature heat capacity have been reported by Simon and Ruhemann [10] (71° to 79°), Lewis [7] (97° to 463°), Cristescu and Simon [1] (10° to 300°), and Hill and Smith [4] (4° to 300°). The values obtained on a sample of 99.5 per cent purity by Hill and Smith [4], which are fairly continuous with the high-temperature measurements by Ginnings, Douglas, and Ball [2] (0° to 900°C), have been adopted. Because of compensating differences, the entropy given by Kelley [6] and NBS C-500 [9] based on measurements before those of Hill and Smith [4] is the same as that adopted. The heat-capacity and entropy values given in Stull and Sinke [11] are the same as those adopted in this compilation.

2. Beryllium Hydride, $(BeH_2)_x$

No heat-capacity data have been found for this substance.

3. Beryllium Oxide, BeO

Heat-capacity measurements made by Günther [2] (76° to 85°) and Kelley [5] (55° to 292°) differ widely. The values reported by Kelley [5] on a sample of 99.6 per cent purity have been adopted. The values given in Kelley [6] and in NBS C-500 [9] are the same as those adopted.

4. Beryllium Hydroxide, $Be(OH)_2$

No heat-capacity data have been found.

5. Beryllium Fluoride, BeF_2

No heat-capacity data have been found.

6. Beryllium Chloride, $BeCl_2$

No heat-capacity data have been found.

7. Beryllium Aluminate, $Be(AlO_2)_2$

No low-temperature heat-capacity data have been found on this substance. Nilson and Pettersson [8] determined the mean heat capacity between 0° and 100°C. This value is given in this tabulation. NBS C-500 [9] lists 25 cal/deg mole for the heat-capacity at 298.16°K.

Heat Capacity, Entropy, and Heat Content Function of Beryllium and Its Compounds at 298.15°K

Chemical Formula	Gram Formula Mass	C_p° cal/deg mole	S° cal/deg mole	$\frac{H_{298.15^\circ K} - H_{0^\circ K}}{298.15}$ cal/deg mole	References
Be	9.013	3.95 ± 0.05	2.28 ± 0.02	1.570 ± 0.005	4
$(BeH_2)_x$	(11.029)x	----	----	----	---
BeO	25.013	6.07 ± 0.05	3.37 ± 0.05	----	5
$Be(OH)_2$	43.029	----	----	----	---
BeF_2	47.013	----	----	----	---
$BeCl_2$	79.927	----	----	----	---
$Be(AlO_2)_2$	126.973	25.4 (mean 0° to 100°C)	----	----	8

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C. Magnesium and Its Compounds

1. Magnesium, Mg

Low-temperature measurements of the heat capacity have been reported by Nernst and Schwers [12] (27° to 94°); Eastman and Rodebush [3] (75° to 289°); Clusius and Vaughen [1] (11° to 228°); Estermann, Friedberg, and Goldman [4] (1.8° to 4.2°); Craig, Krier, Coffer, Bates, and Wallace [2] (12° to 320°); and Logan, Clement, and Jeffers [11] (3° to 13°). The values published by Craig, Krier, Coffer, Bates, and Wallace [2] on a sample of 99.9 per cent purity were adopted after correcting by a factor 1.0041. (Private communication from Professor R. S. Craig). The values of entropy based on earlier measurements given in Kelley [7] and NBS C-500 [14] do not differ significantly from the new value; the heat capacities, however, differ considerably. Stull and Sinke [16], give the same values as those adopted in this compilation.

2. Magnesium Hydride, MgH_2

Stull and colleagues [15] (25° to 300°) determined the heat capacity of a sample containing approximately seven per cent free magnesium metal. Their values of heat capacity and entropy have been adopted.

3. Magnesium Oxide, MgO

Günther [6] (21° to 83°), Parks and Kelley [13] (94° to 291°), and Giauque and Archibald [5] (20° to 301°) measured the heat capacity. The former two groups of investigators measured fused samples, while the latter group investigated finely divided MgO prepared by dehydrating $Mg(OH)_2$. The entropies of the substance in the two physical states differ considerably. Separate values of the heat capacity and entropy have been adopted for micro- and macro-crystalline states. Kelley [7] gives an average entropy of the two physical states; the heat capacity is that obtained by Giauque and Archibald [5]. NBS C-500 [14] gives the same separate values as those given in this compilation.

4. Magnesium Hydroxide, $Mg(OH)_2$

Giauque and Archibald [5] (22° to 321°) measured the heat capacity of $Mg(OH)_2$ crystals (average diameter of 0.2 mm) prepared by treating magnesium chloride solution with potassium hydroxide. Their values for the heat capacity and entropy were adopted. Kelley [7] and NBS C-500 [14] give the same values.

5. Magnesium Fluoride, MgF_2

Todd [17] (54° to 297°) measured the heat capacity of a sample prepared by treating MgO with hydrofluoric acid (48% HF) and by drying at 400°C. The material was found to contain 99.87 per cent of theoretical magnesium. Values of heat capacity and entropy reported by Todd [15] were adopted. Kelley [7] and NBS C-500 [14] give the same values.

6. Magnesium Chloride, $MgCl_2$

Kelley and Moore [8] (53° to 295°) measured the heat capacity of a sample prepared by treating magnesium-ammonium chloride hexahydrate with dry HCl up to temperatures of 600°C. The analysis of the product was 100.78 and 99.72 per cent of the theoretical magnesium and chlorine, respectively. MgO was estimated to be present to the extent of 0.2 per cent. Corrections had been applied for this in the heat-capacity results. The values of heat capacity and entropy reported by Kelley and Moore [8] were adopted. Kelley [7] and NBS C-500 [14] give the same values.

7. Magnesium Chloride Monohydrate, $MgCl_2 \cdot H_2O$

Kelley and Moore [9] (53° to 298°) measured the heat capacity of monohydrate of $MgCl_2$ prepared by heating for 16 hours at 120° to 140°C a degassed and sealed stoichiometric mixture of dehydrated and anhydrous magnesium chloride. The material contained 100.47 and 99.71 per cent of the theoretical Mg and Cl, respectively. The MgO content was estimated to be 0.14 per cent. The values of heat capacity and entropy found by Kelley and Moore [9] have been adopted. Kelley [7] and NBS C-500 [14] give the same values.

8. Magnesium Chloride Dihydrate, $MgCl_2 \cdot 2H_2O$

Kelley and Moore [9] (54° to 295°) determined the heat capacity of magnesium chloride-dihydrate prepared by dehydrating a previously prepared sample of tetrahydrate in a stream of dry HCl at 170° to 220°. When the sample was found on analysis to be slightly deficient in water, it was degassed and sealed with a necessary amount of water and "aged" by heating at about 103°C for seven hours. The product was found to have 100.49 and 100.02 per cent of the theoretical Mg and Cl, respectively. The values of heat capacity and entropy found by Kelley and Moore [9] have been adopted. Kelley [7] and NBS C-500 [14] give the same values.

9. Magnesium Chloride Tetrahydrate, $MgCl_2 \cdot 4H_2O$

Kelley and Moore [9] (54° to 296°) measured the heat capacity of the tetrahydrate of $MgCl_2$ prepared by heating the hexahydrate in air in an oven at 100° to 103°C for six days. The product was found to be 100.48 and

100.00 per cent of the theoretical Mg and Cl, respectively. The values of heat capacity and entropy adopted from the work of Kelley and Moore [9] are the same as those given in Kelley [7] and NBS C-500 [14].

10. Magnesium Chloride Hexahydrate, $MgCl_2 \cdot 6H_2O$

Kelley and Moore [9] (54° to 296°) measured the heat capacity of the hexahydrate of magnesium chloride prepared from a reagent-grade material. The excess water that was present was removed by storing over 80 per cent sulfuric acid at room temperature for seven days. The product was found to contain 100.75 and 99.80 per cent of the theoretical Mg and Cl, respectively. The values of heat capacity and entropy adopted from the work of Kelley and Moore [9] are the same as those given in Kelley [7] and NBS C-500 [14].

11. Magnesium Hydroxy Chloride, $Mg(OH)Cl$

No low-temperature heat-capacity data have been found. The value of entropy was adopted from that given in NBS C-500 [14] which was calculated from heat and free energy of formation.

12. Magnesium Aluminate, $MgO \cdot Al_2O_3$

King [10] (53° to 296°) measured the heat capacity of $MgO \cdot Al_2O_3$, prepared by heating for periods totaling 15 hours at 1480° to 1500°C, a stoichiometric mixture of reagent-grade magnesia and pure hydrated alumina. The analysis of the product showed 99.94 and 99.96 per cent theoretical Al_2O_3 and MgO, respectively. Values of heat capacity and entropy were adopted from the work of King [10]. Kelley [7] and NBS C-500 [14] do not list any values for these properties of this substance.

Heat Capacity, Entropy, and Heat Content Function of Magnesium and Its Compounds at 298.15°K

Chemical Formula	Gram Formula Mass	C°_p cal/deg mole	S° cal/deg mole	$\frac{H_{298.15^\circ K} - H_{0^\circ K}}{298.15}$ cal/deg mole	References
Mg	24.32	5.95 ± 0.03	7.81 ± 0.05	----	2
MgH_2	26.336	8.44 ± 0.20	7.49 ± 0.10	----	15
MgO	40.32	8.94 ± 0.03 Macro-crystal	6.4 ± 0.1	----	13
		9.03 ± 0.03 Micro-crystal	6.66 ± 0.10	----	5
$Mg(OH)_2$	58.336	18.41 ± 0.04	15.09 ± 0.05	----	5
MgF_2	62.32	14.72 ± 0.04	13.68 ± 0.07	----	17
$MgCl_2$	95.234	17.00 ± 0.05	21.4 ± 0.2	----	8
$MgCl_2 \cdot H_2O$	113.250	27.52 ± 0.08	32.8 ± 0.5	----	9
$MgCl_2 \cdot 2H_2O$	131.266	38.05 ± 0.10	43.0 ± 0.5	----	9
$MgCl_2 \cdot 4H_2O$	167.298	57.68 ± 0.20	63.1 ± 0.7	----	9
$MgCl_2 \cdot 6H_2O$	203.330	75.37 ± 0.40	87.5 ± 1.0	----	9
$Mg(OH)Cl$	76.785	----	19.8	----	14
$MgO \cdot Al_2O_3$	142.280	27.71 ± 0.08	19.26 ± 0.10	----	10

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D. Lithium and Its Compounds

1. Lithium, Li

Measurements of the low-temperature heat capacity have been published by Simon and Swain [20] (15° to 300°) and Roberts [16] (1.5° to 20°). The results obtained by Simon and Swain [20] do not show continuity with the more recent heat-capacity values derived from the heat-content measurements in the range 0° to 900°C by Douglas, Epstein, Dever, and Howland [8]. At 300°K the heat-capacity value obtained by Simon and Swain is 4 per cent lower than that obtained by Douglas et al. The values of heat capacity, entropy, and heat-content function adopted have been taken from the work of Douglas, et al [8] in which these values were recalculated after adjusting the values of heat capacity obtained by Simon and Swain [20]. The values based only on the work by Simon and Swain [20] given in Kelley [13] and NBS C-500 [17] differ somewhat from those adopted. Stull and Sinke [22] and Evans, Jacobson, Munson, and Wagman [9] give values essentially the same as those adopted in this compilation. Because of relatively large uncertainties, additional experimental work on this substance may be required. There are some unpublished measurements which are not as yet available.

2. Lithium Hydride, LiH

Günther [10] (74° to 293°) measured the heat capacity of a lithium hydride sample which was apparently not completely hydrided. The measurements were clustered between 74° and 91°K and a single point obtained at 293°K. Kelley [13] and NBS C-500 [17] give the same values of heat capacity and entropy based on Günther's work. The same values have been adopted tentatively in this compilation. New measurements are required to reduce the uncertainty.

3. Lithium Oxide, Li_2O

Measurements of the heat capacity have been reported by Johnston and Bauer [11] (17° to 299°) on a sample prepared by heating purified crystals of $LiOH \cdot H_2O$ up to temperatures as high as 1300°C. On the basis of hydrochloric acid titration and spectroscopic analysis, the sample was taken to be 99.74 per cent Li_2O and 0.26 per cent CaO. The values of the heat capacity obtained by Johnston and Bauer [11] are continuous with those derived from the heat-content measurements by Shomate and Cohen [19]. The values of heat capacity, entropy, and heat content function were adopted from the work of Johnston and Bauer [11]. Kelley [13] and NBS C-500 [17] do not list any values for the properties of this substance.

4. Lithium Hydroxide, LiOH

Bauer, Johnston, and Kerr [1] (15° to 303°) measured the heat capacity of LiOH prepared from purified crystals of $LiOH \cdot H_2O$ by heating at 150°C in a stream of CO_2-free air. Hydrochloric acid titration showed the purity to be 99.9 ± 0.2 per cent. Values of heat capacity, entropy, and heat content function were adopted from the work of Bauer et al [1]. Kelley [13] and NBS C-500 [17] list an entropy value calculated from heat and free energy of formation which is approximately 1 e.u. higher than that adopted in this compilation.

5. Lithium Hydroxide Monohydrate, $LiOH \cdot H_2O$

Low-temperature measurements of the heat capacity were made by Bauer, Johnston, and Kerr [1] (15° to 302°) on a sample purified by crystallization from water. The excess water was removed by dessicating over anhydrous LiOH. Hydrochloric-acid titration showed the sample to have Li to H_2O ratio of 0.9993 ± 0.0027. The values of heat capacity, entropy, and heat-content function from this work by Bauer et al [1] were adopted. Kelley [13] does not list values for these properties of the substance. NBS C-500 [17] lists a considerably higher value for the entropy calculated from the heat and free energy of formation.

6. Lithium Fluoride, LiF

Measurements of the low-temperature heat capacity of lithium fluoride have been reported by Clusius [2] (18° to 273°); Clusius, Goldmann, and Perlick [4] (18° to 272°); Martin [15] (2° to 30°); Clusius and Eichenauer [3] (10° to 111°); and Scales [18] (2° to 7°). The results of all of the above measurements, where tabulated values or equations of heat capacity are available for comparison, show good agreement and are continuous with the heat-capacity values derived from the heat-content measurements in the range 0° to 900°C by Douglas and Dever [7]. The values of heat capacity and entropy in this compilation have been adopted from the work by Douglas and Dever [7] in which these values were computed from the measurements of Clusius, Goldmann, and Perlick [4]. Kelley [13] gives values somewhat lower because of inadvertent use of C_v values given in Clusius [2]. The values given in NBS C-500 [17] are essentially the same as those adopted in this compilation. The value of entropy tabulated by Voskrensenskaya, Sokolov, Banashek, and Schmidt [23] is essentially the same as that adopted, but their heat capacity is somewhat lower.

7. Lithium Chloride, LiCl

No low-temperature heat-capacity measurements have been found on this substance. Slonim and Hüttig [21] have published mean heat capacity measurements (-188° to -77°C, -77° to -3°C, and 4° to 96°C). Recently, Douglas [6] determined the heat content relative to 0°C of LiCl up to 900°C and derived the heat capacity at 298.15°K to be 11.57 cal/deg mole. This value was adopted for the heat capacity. Kelley [12] gives 12.0 cal/deg mole. The entropy, which was calculated from the heat and free energy of formation, was taken from Kelley [13].

8. Lithium Chloride Monohydrate, $LiCl \cdot H_2O$

No low temperature heat-capacity data have been found on this substance. Slonim and Hüttig [21] have published mean heat-capacity measurements (-188° to -77°C, -77° to -3.3°C, and 6.0° to 86.8°C). The values of heat capacity and entropy were adopted from NBS C-500 [17], in which the entropy was obtained from heat and free energy of formation.

9. Lithium Aluminum Hydride, $LiAlH_4$

No low temperature heat-capacity data have been found on this substance. Davis, Mason, and Stegeman [5] reported the specific heat at 25°C to be 0.48 ± 0.01 cal/deg gm (18.2 ± 0.4 cal/deg mole). The same value is given in NBS C-500 [17].

10. Lithium Aluminate, $LiAlO_2$

King [14] (52° to 296°) measured the heat capacity of lithium aluminate prepared by heating a stoichiometric mixture of reagent-grade lithium carbonate and pure hydrated alumina for periods totaling 50 hours at 900° to 1000°C. Chemical analysis of the product showed 100.03 per cent of the theoretical Al_2O_3 to be present. Values of heat capacity and entropy were adopted from the work by King [14]. Kelley [13] and NBS C-500 [17] do not list these properties for this substance.

Heat Capacity, Entropy, and Heat Content Function of Lithium and Its Compounds at 298.15°K

Chemical Formula	Gram Formula Mass	C_p^o cal/deg mole	S^o cal/deg mole	$\frac{H_{298.15°K} - H_{0°K}}{298.15}$ cal/deg mole	References
Li	6.940	5.89 ± 0.20	6.78 ± 0.07	3.66 ± 0.03	8
LiH	7.948	8.3 ± 0.5	5.9 ± 0.5	----	13, 17
Li_2O	29.880	12.93 ± 0.03	9.06 ± 0.03	5.81 ± 0.02	11
LiOH	23.948	11.85 ± 0.03	10.23 ± 0.05	5.94 ± 0.02	1
$LiOH . H_2O$	41.964	19.00 ± 0.04	17.07 ± 0.05	9.74 ± 0.03	1
LiF	25.940	10.01 ± 0.02	8.52 ± 0.08	----	7
LiCl	42.397	11.57 ± 0.05	13.9 ± 0.5	----	6, 13
$LiCl . H_2O$	60.413	23.4	24.8	----	17
$LiAlH_4$	37.952	18.2 ± 0.4	----	----	5
$LiAlO_2$	65.920	16.20 ± 0.05	12.7 ± 0.1	----	14

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CHAPTER III

HIGH-TEMPERATURE HEAT CONTENT

T. B. Douglas and A. C. Victor

This chapter is arranged into four sections according to the compounds aluminum, beryllium, magnesium and lithium, respectively. A critical discussion of literature data is given in each section, and the heat-content data for all compounds are tabulated in table 1. The procedure followed is to express the heat content in the form of the equation $H_T - H_{298.15} = AT + BT^2 + CT^{-1} + D \log_{10} T + E$ defined calories per gram-formula-weight at T°K (1 defined cal. = 4.1840 abs. joules), and to give the values of these constants in the table. In those cases where all the constants except A are given as zero, the temperature coefficient of the heat capacity is zero within the accuracy of the data. These equations are numbered in the table to permit reference to them in the text which follows. The formula weight is based on the International Atomic Weights of 1956. The stated temperature range in each case is that over which the equation is considered to give as reliable thermal values as the data do themselves. In the designation of state, "c" refers to crystalline, "l" to liquid, and "c + l" to the melting point and the measured heat of fusion.

The estimated mean accuracy given in the last column of table 1 applies to the heat content relative to that at 298°K. Although some attempt has been made to reflect in these uncertainties the probability of systematic error, in many cases it is clearly impossible to do more than repeat the investigator's estimate. However, in the case of every substance for which a value of the heat capacity at 298°K is represented in both this chapter and the preceding one, the two values agree within the estimated uncertainty, and in most of these cases the indicated variation of heat capacity with temperature (at 298°K) also agrees.

A. Aluminum and Its Compounds

1. Free Element. The most recent data available on Al were compiled by Stull and Sinke [1] and come directly from the equations given here, which were derived by Kelley [2]. In the solid state (298.15° - 931.7°K) equation 1, given in table 1, fits the data to ± 0.5%. In the liquid region the data are represented up to 1300°K within ± 2% by equation 3.

The melting temperature is well established at 932 ± 1°K. Kelley [2] compiled a more specific value of 931.7°K and heat of fusion of 2.57 ± 0.1 Kcal/mole. Kubaschewski et al [3] determined a heat of fusion of 2.50 ± 0.05. The more recent determinations of Oelson and coworkers [4,5] yield values of the heat of fusion of 2.63 ± 0.03 and 2.66 ± 0.05 Kcal/mole, respectively. The value chosen by Kelley seems to cover all measurements quite well.

Table 1. Heat Content of Condensed Phases above 298°K

$H_T - H_{298.15} = AT + BT^2 + CT^{-1} + D\log_{10}T + E$; defined cal/g formula wt; (T in °K)

Formula	Eq. no.	State	Temp. range °K	A	B	C	D	E	Est. mean accuracy % of ΔH
Al	1	c	298–932	4.94	$1.48(10^{-3})$	0	0	−1605	± 0.5
Al	2	c+l	932 ± 1	Heat of fusion = 2570					± 4
Al	3	l	932–1300	7.00	0	0	0	+330	± 2
Al_2O_3	4	c(α)	298–400	See table 2					± 0.2
Al_2O_3	5	c(α)	400–1200	35.51	$-4.088(10^{-4})$	0	−11232	+17240	± 0.2
Al_2O_3	6	c(α)	1200–1800	27.43	$1.53(10^{-3})$	$8.47(10^5)$	0	−11155	± 1
$Al_2O_3 \cdot H_2O$	7	c	298–500	28.87	$4.20(10^{-3})$	0	0 (e)	−8981	± 5
$Al_2O_3 \cdot 3H_2O$	8	c	298–425	17.30	$45.6(10^{-3})$	0	0	−9212	± 2
AlF_3	9	c(α)	298–727	17.27	$5.48(10^{-3})$	$2.30(10^5)$	0 (f)	−6408	± 0.5
AlF_3	10	c(β)	727–1400	20.93	$1.50(10^{-3})$	0	0 (f)	−6500	± 0.5
$AlCl_3$	11	c	298–465.6	13.25	$14.00(10^{-3})$	0	0	−5195	± 2
$AlCl_3$	12	c+l	465.6	Heat of fusion = 8500					± 2
$AlCl_3$	13	l	465.6–500	31.2	0	0	0	−2018	± 2
Be	14	c	367–1170	See table 3					± 1
Be	15	c+l	1556 ± 1	Heat of fusion = 2800					± 20
Be	16	l	1556→	7.50	0	0	0	E[(a)]	
BeO	17	c	298–1200	14.088	$4.878(10^{-5})$	0[(b)]	−5548.7	9522.88	± 0.3
Mg	18	c	298–923	4.689	$1.718(10^{-3})$	$-2.0776(10^4)$	0	−1481	± 1
Mg	19	c+l	923	Heat of fusion = 2140					± 2.3
Mg	20	l	923–1100	5.292	$1.30(10^{-3})$	$1.179(10^4)$	0	409.8	± 1
MgO	21	c	298–1200	13.7146	$-2.247(10^{-5})$	0	−3267.1	3997.2	± 0.3
$Mg(OH)_2$	22	c	298–600	10.981	$9.3(10^{-3})$	$-1.71(10^5)$ (e)	0 (d)	−3527	± 3
MgF_2	23	c	298–1536	17.125	$1.189(10^{-3})$	$2.7996(10^5)$	0 (d)	−6150	± 1
MgF_2	24	c+l	1536	Heat of fusion = 13900					± 0.5
MgF_2	25	l	1536–1800	22.57	0	0	0	2450	± 0.5
$MgCl_2$	26	c	298–987	18.90	$0.71(10^{-3})$	$2.06(10^5)$	0	−6390	± 0.5
$MgCl_2$	27	c+l	987	Heat of fusion = 10300					± 0.5
$MgCl_2$	28	l	987–1500	22.10	0	0	0	1650	± 0.5

Continued

Table 1. (cont'd) Heat Content of Condensed Phases above 298°K

$H_T - H_{298.15} = AT + BT^2 + CT^{-1} + D \log_{10}T + E$; defined cal/g formula wt; (T in °K)

Formula	Eq. no.	State	Temp. range °K	A	B	C	D	E	Est. mean accuracy % of ΔH
Li	29	c	298–453.7	See table 4.					± 0.5
Li	30	c+l	453.7		Heat of fusion = 717				± 0.5
Li	31	l	453.7–1200						± 0.5
Li_2O	32	c	298–1050	14.939	$3.04(10^{-3})$	$3.38\ (10^5)$	0	-5858	± 1
LiOH	33	c	298–744.3	11.988	$4.12(10^{-3})$	$2.26\ (10^5)$	0	-4701	± 1
LiOH	34	c+l	744.3	Heat of fusion = 5010					± 1
LiOH	35	l	744.3–900	20.74	0	0	0	-3638	± 1
LiF	36	c	298–1121	See table 5.					± 0.5
LiF	37	c+l	1121.3	Heat of fusion = 6470					± 0.5
LiF	38	l	1121.3–1400	15.31	0	0	0	-180	± 1
LiCl	39	c	298–880	10.9036	$2.2944(10^{-3})$	0	-484.89	-2255.2	± 0.5
LiCl	40	c+l	880	Heat of fusion = 4715					± 0.5
LiCl	41	l	880–1200	17.0691	$-7.6(10^{-4})$	0	0	-2028.3	± 0.5

(a) Value for C_p = 7.50 cal/mole given but no constant for evaluating the enthalpy.
(b) An additional term $[+(22.99\ T - 6280.4)_e\ -0.01842T]$ appears in BeO eq.(14). Effect of term is negligible above 500°K.
(c) For macrocrystalline MgO C_p = 8.94 ± 0.03, for microcrystalline C_p = 9.03 ± 0.03. The high temperature measurements were on large crystals.
(d) High-temperature data have been adjusted to fit low temperature C_p at 298.15°K.
(e) Equations 7 and 22 do not permit smooth joining of low and high temperature C_p values.
(f) Heat of transition (727°K) = 150.

2. Oxides. The heat content of α-Al_2O_3 has been accurately measured at the National Bureau of Standards [6] up to 1200°K. The results of this work are selected as the most reliable in this temperature range, and are represented from 400° to 1200°K by equation 5. In the temperature range from 298.15° to 400°K the chosen values deviate from the equation. Adopted values between 298.15 and 400°K are given in Table 2. These values and the equation are believed to be accurate to ± 0.2%.

Shomate and Naylor [9] measured the heat content of α-Al_2O_3 up to 1800°K, and these results are chosen to represent the range from 1200° to 1800°K (eq. 6). This equation fits the NBS data to better than ± 0.1% at 1000° and 1200°K. However an extrapolation of the NBS equation to 1800°K yields a value for heat content which is 0.9% lower than that obtained by Shomate and Naylor. Other apparently reliable work on Al_2O_3 includes that of Olette [7], Margrave and Grimley [8], Shomate and Cohen [10], and Rodigina and Gomelskii [11].

3. Hydroxides. The only reported measurements on the heat content of hydrated aluminum oxide were made by Shomate and Cook [12], who obtained values represented by eq. 7 and 8. The values for the monohydrate are probably reliable to ± 5%, and those for the trihydrate, to ± 2%.

4. Fluoride. The most recent data for the heat content of AlF_3 were obtained by O'Brien and Kelley [13]. They found a minor crystalline transformation at 727°K with a heat effect of only 150 cal/mole; otherwise their data agree with those of Lyashenko [14] to ± 0.8%.

The chosen values fit equations 9 and 10 at the indicated temperatures with the mean percentage deviations indicated.

5. Chloride. The data of Fischer [15] for $AlCl_3$ yield equations 11 and 13, which fit the data to ± 2%. A heat of fusion of 8.50 Kcal/mole at 465.6°K is obtained. No other data were found.

B. Beryllium and Its Compounds

1. Free Element. The most reliable data for Be seem to be those of Ginnings, Douglas and Ball [16]. Their data are given in Table 3. The melting point has been reported as 1556° ± 1°K in the compilations of Kubaschewski and Evans [17], Kubaschewski et al [3], and Rossini, Wagman, Evans, Levine, and Jaffe [18]. Kubaschewski and coworkers [3] give 2.8 ± 0.5 Kcal/mole as the heat of fusion at 1556°K.

In the liquid region Kelley [19] has adopted a constant heat capacity, viz.

$$C_p = 7.50 \text{ cal deg}^{-1} \text{ mole}^{-1}.$$

Table 2. Heat Content of α-Al_2O_3 from 298 - 400°K

T °K	$H_T - H_{298.15}$ cal/mole	T °K	$H_T - H_{298.15}$ cal/mole
298.15	0	360	1257.4
300	34.9	380	1697
320	424.5	400	2151
340	832.4		

Table 3. Heat Content of Be from 367 - 1170°K

T °K	$H_T - H_{273.15}$ cal/mole	T °K	$H_T - H_{273.15}$ cal/mole
367.15	384.5	870.75	3184
468.95	879	972.85	3831
571.45	1425	1070.05	4470
667.75	1970	1169.55	5147
770.95	2576		

2. Oxide. The heat-content data of Victor and Douglas [20] have been adopted as the most reliable. Equation 17 fits the data to ± 0.1% in the range from 298° to 1500°K, with an estimated accuracy of ± 0.3%. These values average about 0.5% higher than those reported by Kelley [2].

3. Hydroxide, Fluoride, Chloride. No data were found for the hydroxide, fluoride or chloride of beryllium.

C. Magnesium and Its Compounds

1. Free Element. The most recent high-temperature heat-content data were obtained by Saba, Sterret, Craig, and Wallace [31] in the range from 298° to 543°K. These results join smoothly with the low temperature work of Craig, Krier, Coffer, Bates and Wallace [32]. Stull and McDonald [21] measured the heat content of Mg between 700° and 1100°K, and Seekamp [22] from 290° to 770°K. Here the data of Saba et al. and Stull and McDonald (loc. cit.) have been joined to give the heat-content equation 18. The equation is believed accurate for the solid to ± 1%. The heat content values obtained from equation 18 are in general lower by from 0.3% to 1.2% than those reported by Stull and Sinke [1], the smaller deviation occuring at the higher temperatures. Stull and McDonald [21] obtained a heat of fusion of 2.14 ± 0.05 cal/mole at the melting point, 923°K. Above 923°K the liquid heat content of Stull and McDonald [21] has been adopted and assumed to apply up to 1300°K. (The authors indicated this extrapolation and it probably does not introduce any great uncertainty.) Equation 20 fits the experimental data to ± 0.7% in the liquid region 923 - 1100°K.

2. Oxides. The high-temperature heat content of single-crystal magnesium oxide has been measured by Victor and Douglas [20] up to 1200°K. The results fit equation 21 to better than ± 0.1%. This equation joins well at 298°K with the low temperature data of Parks and Kelley [23], who also investigated single-crystal MgO. The heat capacity values for powdered MgO obtained by Giauque and Archibald [24] at low temperatures are higher by 1% at 298°K than those of the single-crystal specimen.

Kelley's compilation [2] of heat-content data gave greatest weight to the work of Magnus [25] and Wilkes [26], and gives values of heat content which range from 1.5 to 4.5% lower than those given above [20]. The more recent work of Arthur [27] is uncertain by ± 2%. Wilkes made measurements up to 2100°K; it is of interest that an extrapolation to 2100°K of the equation obtained by Victor and Douglas [20] fits Wilkes' data within the precision of the latter.

3. Hydroxide. The heat content of $Mg(OH)_2$ was reported by Lashchenko and Kompanskii [28]. Equation 22 can be used to represent their data to ± 3% from 298° to 600°K.

4. **Fluoride.** Naylor [29] measured the heat content of MgF_2 and obtained equations 23 and 25. From them a heat of fusion of 13.9 ± 0.07 Kcal/mole at the melting point, 1536°K, is obtained.

5. **Chloride.** Moore [30] measured the heat content of $MgCl_2$ and obtained the equations26 and 28. The heat of fusion from this investigation is reported as 10.3 ± 0.05 Kcal/mole at 987°K, the melting point.

D. Lithium and Its Compounds

1. **Free Element.** The most careful heat-content study of Li was made by Douglas et at [33], and their results are given up to 1200°K in table 4. The accuracy of the data is estimated to be ± 0.5%. A heat of fusion of 7170 cal/g atom at 453.7°K was reported.

2. **Oxide.** The heat content of Li_2O was measured up to 1050°K by Shomate and Cohen [34]. The results are reported in equation 32, and are probably accurate to better than ± 1%.

3. **Hydroxide.** Shomate and Cohen [34] reported the heat content of solid LiOH (298° - 744.3°K) (eq. 33) and liquid LiOH (744.3° - 900°K) (eq. 35), and a heat of fusion of 5010 cal/mole at 744.3°K.

4. **Fluoride.** Precise heat-content data (298° - 1200°K) for LiF were reported by Douglas and Dever [35], and are given in table 5. Voskresenskaya et al [37] made measurements up to 1400°K. Combination of both workers results above 1121°K gives equation 38 for the heat content of the liquid.

Both workers report a heat of fusion of 6470 cal/mole at 1121.3°K. The liquid heat capacity is uncertain by ± 2% or more. This would correspond to an uncertainty in relative heat content ($H_T - H_{298.16}$) at these temperatures of not more than ± 1%.

5. **Chloride.** The only data on the heat content of LiCl was obtained by Douglas et al [36] from 298° - 1173°K, and are given in equations 39 and 41. They reported a heat of fusion of 4715 cal/mole at 880°K. They measured two samples; these were only 98 and 99 mole % pure, respectively, but on the basis of accurate chemical analyses the impurities were corrected for. The resulting heat capacities for the two samples agreed almost exactly in the solid range, and to about 0.2% in the liquid range.

Table 4. Thermodynamic Functions of Li (mole wt = 6.940)
cal/deg. g. atom

T °K	$C_p°$	S°	$\frac{H° - H_0°}{T}$	$-\frac{F° - H_0°}{T}$
298.15	5.892	6.777	3.656	3.121
300	5.899	6.814	3.670	3.144
400	6.599	8.596	4.306	4.290
453.7 (s)	7.022	9.455	4.604	4.851
453.7 (l)	7.264	11.035	6.184	4.851
500	7.200	11.738	6.281	5.457
600	7.060	13.038	6.422	6.616
700	6.928	14.116	6.504	7.612
800	6.916	15.041	6.556	8.485
900	6.904	15.854	6.595	9.259
1000	6.892	16.581	6.626	9.955
1100	6.880	17.238	6.649	10.589
1200	6.868	17.836	6.668	11.168

Table 5. Thermodynamic Functions of LiF (mole wt = 25.94)

cal/deg mole

T °K	$C_p°$	S°	$\frac{H° - H°_{298.15}}{T}$	$-\frac{F° - H°_{298.15}}{T}$
298.15	10.015	8.52	0	8.52
300	10.042	8.582	0.062	8.520
400	11.142	11.636	2.707	8.929
500	11.831	14.201	4.467	9.734
600	12.336	16.404	5.738	10.666
700	12.770	18.339	6.712	11.627
800	13.200	20.072	7.496	12.576
900	13.677	21.654	8.156	13.498
1000	14.239	23.123	8.735	14.388
1100	14.921	24.511	9.265	15.246
1121.3 (s)	15.085	24.798	9.374	15.424
1121.3 (l)	15.51	30.569	15.145	15.424

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CHAPTER IV

MOLECULAR CONSTANTS FROM SPECTROSCOPIC DATA AND OTHER SOURCES

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A. Introduction

Selected values of the molecular constants for gaseous molecules of Li, Be, Mg, and Al, in their ground electronic states are listed in Tables 1 to 4 found at the end of the chapter and discussed below in Sections B and C. Also tabulated are constants for Li_2, F_2, Cl_2, ClF, and ClO.

The constants for diatomic molecules were taken from the compilations of Rosen [1]* and Herzberg [2] except in those cases where more recent experimental data were available. Where several band systems were studied, the average value for the ground state has been tabulated.

Spectroscopic and molecular constants not contained in the literature for the molecules discussed herein were estimated or computed from other data in various ways and, except where otherwise noted, included in parentheses in the tables. The constants for most of the polyatomic molecules are largely estimated values due to the lack of the requisite experimental data. This is particularly true for the aluminum compounds listed in Table 4.

All calculated constants for the diatomic molecules are weighted mean values consistent with the relevant natural isotopic abundances. The symbols for molecular constants used throughout the chapter have their usual significance as defined by Herzberg [2].

B. Diatomic Molecules

1. Dimers of Light-Metal Atoms (Table 1). Molecular constants for Li_2 have been derived from the spectroscopic data given by Rosen [1] for $^7Li_2$ and $^7Li^6Li$ and adjusted for the normal isotopic abundance. Few data have been reported for homonuclear diatomic molecules of the other

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*Numbers in brackets refer to the list of references included at the end of the text.

metals.[*] However, the band spectrum of Mg_2 has been observed both in absorption [3] and emission [4], but as yet no complete analysis of the band systems has been made.

2. Halides of Li, Be, Mg, and Al (Table 1). The fundamental vibrational frequencies for lithium fluoride and lithium chloride were obtained from the recent infrared spectral data of Klemperer [5]. Values for the rotational constant, B_e, were computed from estimated values of the moments of inertia. The moments of inertia for LiF and LiCl, shown in the table below, were calculated from internuclear distances deduced by Honig, et al [6] from a correlation of r_e values, accurately determined by microwave spectroscopy, for 15 other alkali halides.

	$10^{39}I$ (gm cm^2)	r_e (A)
LiF	1.968	1.527
LiCl	3.940	2.022

The quantity $\omega_e x_e$ for LiF and LiCl was estimated from the ratio $4D_e(\omega_e x_e)/\omega_e^2$ [**] which was assumed to have a value of 1.6 in each case. (This ratio was found to vary from 1.0 to 1.9 for seven other alkali halide molecules, e.g. 1.9 for LiBr and 1.5 for LiI.)

A mean value of 1.32 for the ratio $\alpha_e \omega_e / B_e(\omega_e x_e)$ was used to estimate α_e for LiF and LiCl.[***] (The value of this ratio ranged from 1.26 to 1.38 for 9 other alkali halide molecules, including LiBr and LiI).

Spectroscopic constants for the ground electronic states of the diatomic fluorides and chlorides of Be, Mg, and Al, except for AlF, were taken from the compilations of Rosen and Herzberg. The more recent data of Naudé and Hugo [8], and Barrow and Rowlinson [9] for AlF have been used. The rotational constant, B_e, has not been measured accurately for BeCl and MgCl; consequently, values have been calculated on the assumption that the bond distances are the same as those for the corresponding dihalides [10]. The constants α_e and D_e have been calculated by the usual formulas [2] in instances where experimental values were not available.

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[*] Dissociation energies for Al_2 and Be_2 have been reported and are discussed in Chapter VI.

[**] D_e = dissociation energy.

[***] Values of $\omega_e x_e$ for LiF and LiCl calculated from these estimated values of α_e, assuming a Morse-function oscillator in the neighborhood of the potential minimum [7], were in agreement with those deduced from the ratio, $4D_e(\omega_e x_e)/\omega_e^2$, within about 10 per cent.

3. Oxides of Be, Mg, and Al (Table 1). The molecular constants for BeO and MgO are those given in Rosen [1] and Herzberg [2]. New data for AlO* have recently appeared in the literature [11].

For MgO, there is no certainty that the $^1\Sigma$ state, for which data have been quoted, is the true ground state [1,2,12]. There have been suggestions that the ground state may be $^3\Sigma$. Gaydon [13] has indicated that one observed [14] band system in the MgO spectrum may involve a triplet state.

4. Halogen Molecules and ClO (Table 1). Molecular constants for F_2, Cl_2, and ClF have been selected from a paper by Evans, Munson, and Wagman [15] on the thermodynamic properties of halogen compounds. Some of the constants contained therein are estimates.

The principal constants for ClO are the result of the spectroscopic work of Durie and Ramsay [16], and Porter [17]. The value for α_e has been estimated on the basis of other constants. A value for B_e was obtained from the experimental value for B_0 and the estimated value for α_e.

C. Polyatomic Molecules

1. Dimeric Halides of Lithium (Table 2). Assuming the fundamental frequency of the monomer, LiF, to have the value given in Table 1, the frequencies tabulated for the dimer, Li_2F_2, are those estimated by Porter and Schoonmaker [18] using the methods of Bauer, Diner and Porter [19]. Although these methods of estimating the dimer frequencies are questionable on theoretical grounds, at least they can claim some degree of experimental support by having served as a semi-empirical means for smoothing the dimerization energies evaluated by Miller and Kusch [20] from their molecular beam data.

The moments of inertia tabulated here were calculated theoretically from an ionic model after requiring that the dissociation energy have the value recommended by Porter and Schoonmaker [18]. It should be noted that the heat capacity of the gaseous dimer above room temperature, unlike the entropy, is insensitive to the assumed frequencies and moments of inertia.

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* $r_e = 1.6176A.$

The vibrational frequencies for Li_2Cl_2 are those estimated by Bauer, Diner, and Porter [19]. The reliability of the methods of estimation used have been discussed above under "Li_2F_2." The moments of inertia given here were calculated theoretically from an ionic model. In so doing, the energy of dimerization found by Miller and Kusch [20] was assumed, this energy value being almost identical with that arrived at in the calculations of Bauer, Diner, and Porter [19].

Although reasonable estimates of frequency fundamentals and moments of inertia for the higher LiX polymers might be made by the methods discussed above for the dimers, the uncertainties would be greater; therefore no attempt has been made here to extend the calculations.

2. Dihalides of Be and Mg (Table 3). These molecules are clearly linear [10]. Two of the three fundamentals for BeF_2, $BeCl_2$, and $MgCl_2$ have been measured [21]. The infrared inactive fundamental was assumed to be about 1/2 of ν_3. The fundamentals of MgF_2 were assumed to be in the same ratio to those of $MgCl_2$ as is found for the beryllium compounds. The bond distances in these compounds have been measured accurately by electron diffraction [10], so that the calculated moments of inertia should be reliable to 3 or 4 per cent.

The mixed halides BeFCl and MgFCl have not been reported in the literature. Molecular constants were, however, estimated for them on the basis of the data for BeX_2 and MgX_2.

3. Aluminum Compounds with F, Cl, O and H (Table 4). The molecular constants for the aluminum compounds discussed below have been largely estimated from other data.

There is little doubt that AlF_3 and $AlCl_3$ have planar symmetric structures. The only available vibrational information is Klemperer's measurement [22] of the degenerate stretching fundamental of $AlCl_3$. Using this measurement as a starting point, we have estimated the fundamentals for AlF_3 and $AlCl_3$ by analogy with the boron trihalides (cf Ref. [23]). The resulting values are reasonably in line with the meager information available on solid compounds [24] such as $AlCl_3 \cdot NH_3$ and $NaAlCl_4$.

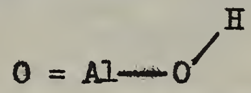
The mixed halides AlF_2Cl and $AlFCl_2$ have not been reported in the literature but they may well exist. Their fundamentals were estimated with the help of the known behavior of mixed boron halides.

The existence of AlF_2 and $AlCl_2$ at high-temperatures has been proposed on the basis of indirect evidence [25]. The tabulated fundamentals were estimated on the basis of the trihalide fundamentals, in conjunction with the reasonable assumption that the vertex angles are about 120°.

In the calculation of the moments of inertia, the Al-F and Al-Cl bond distances were assumed to be 1.70A and 2.10A, respectively.

The oxyhalides AlOF and AlOCl may be stable molecules, although there is no direct evidence for their existence. Their structures have been assumed to be linear; however the arguments for this are rather tenuous, and a bent structure cannot be excluded. Fundamental vibrations and bond distances have been estimated from the values for related molecules.

A provisional choice of constants for AlO_2H has been made on the basis of the following assumed planar structure:



A similar structure seems to be reasonable for BO_2H, in which the OBO part is essentially linear. For AlO, the force constant is definitely greater than it is for single bonds.* The internuclear distance in AlO is 1.6176A which is appreciably less than the sum, 1.92A, of the covalent radii for Al (1.26A) and O (0.66A). The O = Al bond distance in AlO_2H is accordingly taken as 1.62A as in the AlO molecule.

The Al-O single-bond distance in AlO_2H has been assumed to be 1.87A, the smallest of the three AlO bond distances (1.87, 1.88, and 1.99A) found by Milligan and McAtee [27] in crystalline γ-AlO_2H. A considerably shorter AlO single-bond might be expected in the gaseous molecule on the ground that the OH group is similar to the F in electronegativity and, therefore, ionic shortening would be pronounced. For AlF, the sum of the covalent radii is 1.90A (1.26A for Al and 0.64A for F), yet the actual Al-F bond distance is 1.654A.

The O-H bond distance has been assumed to be 0.94A which is intermediate to the O-H distances in such greatly differing molecules as CH_3OH (0.92A), H_2O (0.957A), and OH (0.97A).

The Al-OH bond angle was taken as 105°, which is close to the usual estimate.

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*cf The compilation of force constants prepared by Varshni [26].

The frequencies for AlO_2H were estimated by considering the hydroxyl group as a single lumped mass. The Al-OH bond force constant was assumed to be that of AlF adjusted to a lower value by a factor arbitrarily chosen to be the square-root of the ratio of the force constants for H_2O_2 (assumed to be two lumped OH groups) and F_2 (which has the larger force constant). The O = Al force constant was assumed to be that of the AlO molecule. The resultant calculated frequencies were 680 and 1066 cm^{-1}, which have been rounded to 700 and 1100 cm^{-1}.

The OH stretching and bending frequencies are 3400 and 1200 cm^{-1}, respectively, which are in the range of values for other compounds. The two skeletal bending frequencies have been arbitrarily assigned the values of 500 and 400 cm^{-1} by analogy with values for other compounds.

In the case of AlOH, the bond lengths, bond angle and force constants were given the values estimated for the corresponding parameters in AlO_2H. Molecular constants have also been estimated for the distinctly different molecule, O = AlH. This molecule is thought to be linear. Bond lengths and frequencies have been estimated on the basis of the assumed bond types.

Table 1

Molecular Constants for Diatomic Molecules in Cm^{-1} Units[a]

(Estimated constants are shown in parentheses)

Molecule	Ground State Species	ω_e	$\omega_e x_e$	D_e[c] (x 10^6)	B_e	α_e	References
Li_2[b]	$^1\Sigma_g^+$	353.121	2.627	10.07	0.6796	0.00731	[1]
LiF	$^1\Sigma$	900 ± 30	(7.0)	(14.20)	(1.4221)	(0.015)	[5]
LiCl	$^1\Sigma$	650	(4.3)	3.393	0.7103	(0.0062)	"
BeF	$^2\Sigma$	1265.6	9.12	8.21	1.4877	0.0168	[1,2]
BeCl	$^2\Sigma$	846.6	5.11	(2.5)	(0.766)	(0.007)	"
BeO[b]	$^1\Sigma^+$	1487.19	11.731	8.198	1.6510	0.0190	"
MgF	$^2\Sigma$	717.0	3.84	(1.1)	(0.516)	(0.004)	"
MgCl	$^2\Sigma$	465.4	2.05	(0.25)	(0.245)	(0.001)	"
MgO	$^1\Sigma$(?)	785.06	5.18	1.22	0.5743	0.005	"
AlF	$^1\Sigma$	801.0	4.75	0.97	0.5523	0.0048	[8,9]
AlCl	$^1\Sigma$	481.3	1.95	(0.24)	(0.242)	0.002	[1,2]
AlO	$^2\Sigma^+$	979.23	6.97	1.08	0.6414	0.00580	[11]
F_2	$^1\Sigma_g^+$	919.0	(13.6)	(3.34)	0.8901	(0.0146)	[15]
Cl_2	$^1\Sigma_g^+$	561.0	3.94	(0.1766)	0.2404	0.00166	"
ClF	$^1\Sigma$	784.43	6.20	(0.869)	0.514012	0.0043272	"
ClO	$^2\Pi$	868	7.5	2.2	(0.646)	(0.007)	[16,17]

[a] All calculated constants are weighted values consistent with the relevant natural isotopic abundances.

[b] Vibrational constants have been adjusted to allow for the omission of $\omega_e y_e$.

[c] D_e is here the rotational constant, not the dissociation energy.

Table 2

Molecular Constants for $(LiX)_2$ Species

(Estimated constants are shown in parentheses)

Dimer	ω_1	ω_2	ω_3	ω_4	ω_{5a}	ω_{5b}	σ[c]	I_1[a]	I_2[a]	I_3[a]	Structure[b]
	cm^{-1}							($x\ 10^{39}$), gm cm^2			
$(LiF)_2$	(900)	(555)	(531)	(900)	(531)	(531)	4	11.51	2.455	13.97	P
$(LiCl)_2$	(650)	(318)	(344)	(650)	(344)	(344)	4	39.54	3.314	42.85	P

[a] Based on $Li^+ - X^-$ bond distances of 1.70A for $(LiF)_2$ and 2.19A for $(LiCl)_2$, and $X^- - Li^+ - X^-$ bond angles of 105.2° and 113.6°, respectively.

[b] P = planar.

[c] σ is the symmetry number.

Table 3

Molecular Constants for the Dihalides of Be and Mg

(Estimated constants are shown in parentheses)

Molecule	ω_1	ω_2	ω_3	σ[c]	I ($x\ 10^{39}$) gm cm^2	Structure[a]	Reference
	cm^{-1}						
BeF_2	1520	825(2)	(750)	2	12.36[b]	L	[21]
$BeCl_2$	1113	482(2)	(550)	2	36.06[b]	L	[21]
BeFCl	(1200)	(650)(2)	(800)	1	(20.91)	L	--
MgF_2	(800)	(500)(2)	(400)	2	19.76[b]	L	--
$MgCl_2$	597	295(2)	(300)	2	55.96[b]	L	[21]
MgFCl	(650)	(400)(2)	(450)	1	(33.86)	L	--

[a] L = linear.

[b] Calculated from bond distances measured by electron diffraction [10].

[c] σ is the symmetry number.

Table 4

Molecular Constants for Polyatomic Compounds of Aluminum Containing F, Cl, O and H[a]

Molecule	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	σ[c]	I_a	I_b	I_c	Structure[b]
	cm^{-1}							$(x\ 10^{39})$, gm cm^2			
AlF_3	700	400	900(2)	300(2)	---	---	6	13.67	13.67	27.34	P
$AlCl_3$	350	250	610(2)	150(2)	---	---	6	38.94	38.94	77.88	P
AlF_2	900	700	300	---	---	---	2	1.89	13.67	15.56	B
$AlCl_2$	600	350	150	---	---	---	2	3.58	38.95	42.52	B
AlF_2Cl	850	750	550	350	250	200	2	13.67	27.60	41.27	P
$AlFCl_2$	750	650	450	300	200	150	2	19.57	38.94	58.51	P
O = AlF	900	750	500(2)	---	---	---	1	---	15.48	---	L
O = AlCl	900	450	350(2)	---	---	---	1	---	28.65	---	L
O = AlOH	3400	1200	1100	700	500	400	1	0.13	16.9	17.0	P
O = AlH	1600	1000(2)	900	---	---	---	1	---	5.31	---	L
AlOH	3400	1200	800	---	---	---	1	---	---	---	B

[a] All tabulated constants have been estimated except ω_3 for $AlCl_3$, which has been observed in the infrared [22].

[b] B = Bent, L = Linear, P = Planar.

[c] σ is the symmetry number.

Molecular Constants from Spectroscopic Data and Other Sources

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CHAPTER V

VAPOR PRESSURE AND HEAT OF VAPORIZATION

R. F. Walker, A. C. Victor, and John Efimenko

Introduction

When the thermodynamic properties of substances in the crystalline and liquid states have been established, a study of the equilibria between these condensed phases and the vapor phase furnishes one of the most direct and valuable means of deriving the thermodynamic properties of the gases composing the vapor. Obtaining reliable information on the gases arising from the vaporization of even the most stable oxides of aluminum, beryllium, magnesium, and lithium has presented unusual difficulties for at least two important reasons: (1) These oxides as solids or liquids are highly involatile except at elevated temperatures, and (2) in general the vapors have been found to decompose or associate partially, so that a simple determination of the vapor pressure and its variation with temperature gives no exact and unambiguous data on any one gas species.

This chapter discusses the solid-vapor equilibria involving the two oxides Al_2O_3 and BeO, and presents some of the resulting thermodynamic information. An attempt has been made to take advantage of some of the most recent and most informative research in this field. Treatment of the vaporization of other oxides of the four metals under consideration, as well as other work reported on these two oxides, must be deferred to later reports.

Finally, this chapter presents the results of a recent examination at the Bureau of the consistency between the heats of vaporization of the four free metals and their entropies. Within the uncertainties these independent calculations check the heats of vaporization recently compiled by Stull and Sinke [1]*, which are therefore accepted.

The vapor pressures of the conventional-valence fluorides and chlorides of the four metals have been measured. These results are not discussed here, but in most cases are treated and made use of in the following chapter on heats of formation and dissociation energies. It is now certain that the saturated vapors of LiF, LiCl, $AlCl_3$, and $BeCl_2$ are extensively associated in the range of measurement. The assumption is usually made that the saturated vapors of the other halides such as BeF_2 and AlF_3 are not associated, and thermodynamic properties have then been calculated accordingly. Although this assumption has some support from consideration of the lower volatilities of these halides, it is somewhat open to question in view of the recently discovered evidence for association of the halides first mentioned and the apparent lack of any real positive evidence in the case of the others.

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*See end of this chapter for its references.

The unit of energy used is the defined calorie (= 4.1840 absolute joules).

Vapor Pressures of the Metals Al, Be, Mg and Li

Aluminum. The vapor pressure of aluminum has been measured by Farkas [2] at 1476°K, Baur and Brunner [3] from 1734° to 2237°K, and Brewer and Searcy [4] from 1383° to 1468°K. Earlier measurements were made by Greenwood [16] and von Wartenberg [17]. Johnson et al [5] and Porter, Schissel and Inghram [6] have more recently determined the heat of vaporization using mass spectrometric techniques.

Greenwood and von Wartenberg show considerable deviation from each other and from later workers. The values for the heat of vaporization at 298.15°K found by all the other workers (except Baur and Brunner) lie in the range $\Delta H^{vap}_{298.15} = 78.0 \pm 1$ Kcal/mole. All of these values were obtained from measurements below 1500°K, and there is considerable uncertainty in the vapor density at higher temperatures. Drowart and Honig [18] estimated D_0 of Al_2 gas to be 1.7 e.v. or 39 Kcal/mole. Using this value one might estimate the amount of the dimer in the vapor at various temperatures. This would indicate that the dimer accounts for 1% to 5% of the pressure in the region 1734 - 2237°K measured by Baur and Brunner, and would be about 10% at the estimated boiling point, 2700°K. Waldschmidt [19] has examined the existing vapor pressure data and chosen values of pressure for various temperatures which agree substantially with the work that has been done here. Assuming that workers [2] and [4] made good measurements and had essentially no dimer molecules in their temperature range, one can combine their vapor pressures (extrapolated to higher temperature) with Baur and Brunner's [3] and get a value for D_0 of Al_2 (gas) of about 65 Kcal/mole. However this would give sufficient dimer at 1400°K to have been detected by workers using mass spectrometric techniques. One must conclude that the pressures reported by Baur and Brunner are too high and must be neglected.

The present calculations based on the above data led to

$$H^{vap}_{298.} = 78.0 \pm 1 \text{ Kcal/mole.}$$

$$P - 2000°K = 7.234\ (10^{-3}) \text{ atm.} \qquad [19]$$

This value of H^{vap}_{298} agrees with that adopted in this report, 77.5 kcal/mole [1]

Waldschmidt's [19] vapor pressures were checked by the the 2nd and 3rd law and agree on ΔH^{vap}_{298} within the stated uncertainty.

In all the calculations involved here the values for thermal properties of the condensed phases are those given in Chapters II and III.

Beryllium. Stull and Sinke [1] chose the data of Holden, Speiser and Johnston [7] (1172 - 1552°K) as being the best. These workers give

$$\log P_{atm} = 6.186 + 1.454\ (10^{-4})\ T - \frac{16734 \pm 80}{T}$$

Using the Sackur-Tetrode equation the value of ΔH^{sub}_{298} was calculated to be $\Delta H^{sub}_{298} = 77.68 \pm 0.4$ Kcal/mole. This agrees with the value adopted in this report, 77.9 kcal./mole [1]. Because of uncertainties in the liquid phase thermal values one would probably incur errors of ± 2 Kcal in taking this to the boiling point (assumed to be 2730 ± 100°K).

The gas has been assumed to be all monomer but the 2nd and 3rd law agreement has not been investigated.

Other measurements on Be vapor were made by Baur and Brunner [3] (1850 - 2331°K) and Schuman and Garrett [8] (1150° - 1350°K).

Magnesium. The vapor pressure of liquid magnesium has been measured by Hartmann and Schneider 1012 - 1215°K [9] and by Baur and Brunner 926 - 1283°K [3]. Giving equal weight to these two sets of data, the Second and Third-law methods gave excellent agreement and yielded $\Delta H^{vap}_{298} = 35.45$ kcal/mole ± .3. This agrees with the value adopted in this report, 35.6 kcal/mole [1]. The extrapolated boiling point is 1380°K. Since the vapor pressures of solid magnesium from 626 to 818°K [10] give for ΔH^{vap}_{298} by these two methods much poorer agreement (5%) which cannot be attributed to errors in the thermal values, the data for the solid were given no weight.

Lithium. Based on the heat content work of Douglas et al [11] the vapor pressure measurements of Hartmann and Schneider [9] (1208 - 1353°K), and the spectroscopic analysis of Gordon [12], Loomis [13] and Gaydon [14] the following values for Li would be:

$$\Delta H^{\circ}_{\circ}\ (S \rightarrow \text{monomer gas}) = 37{,}960 \pm 15\ \text{cal/g. at. wt.}$$

at 1350°K; $P_{Li} = 83.2$ mm; $P_{Li_2} = 7.8$ mm. This heat of vaporization is close to that adopted in this report, $\Delta H_{\circ} = 38.05$ or $\Delta H^{\circ}_{298} = 38.44$ kcal./g atomic wt. [1]. Other measurements of Li vapor pressure were made by Maucherat [15] (462 - 642°K) but exhibit considerable scatter. Within their uncertainty however, they do fit the above values.

Condensed and Vapor Phases in the Al-O System

There is no reliable evidence for the existence at high temperature of more than one stable solid phase in the system Al-O. The corundum phase, Al_2O_3, is however, believed to have a fairly wide homogeneity range. The value given in NBS Circular 500 for the melting point of this phase (i.e. 2040°C) is believed to be too high. In fact, values varying from 2000 - 2050°C have been reported over the last few years. The most recent published value [20] lies in the range 2000 - 2030°C. Recent unpublished values [21] are: 2025° and 2025-30°C. The former value was obtained under high-purity conditions using a solar furnace, but is based upon unsubstantiated assumptions concerning the technique of temperature measurement. The latter value was obtained in air using an iridium cell.

The weighted average value of 26 kcals for the heat of fusion of Al_2O_3 may be suspect. This value, given by Kelley [22], is based primarily on data taken from the liquidus curves for the Al_2O_3-TiO_2 system [23], which assumes 2050°C for the melting point of pure Al_2O_3. More recently, a modified version of this diagram has been published. As with approximately 20 other binary phase diagrams having Al_2O_3 as a component, it is not clear from a recent compilation [24] how far the diagram is based on actual measurements in the compositional range of interest. It appears that some of the liquidus curves given at the Al_2O_3 end of the diagrams are merely extrapolations to an assumed melting point of the pure component. An analysis of suitable binary oxide-alumina phase diagrams has been made and the calculated results are shown in Appendix II.

The vapor pressure of aluminum oxide having a composition at the metal-rich end of its homogeneity range appears to be fairly well established [25, 26, 27]. The predominant vapor species appears to be Al_2O. For the reaction $4/3\ Al(l) + 1/3\ Al_2O_3(c) = Al_2O(g)$ Porter et al [27] give $\Delta H^\circ_{1500^\circ K} = 82 \pm 5$ kcals. The data of Brewer and Searcy [25] yield $\Delta H^\circ_{1500^\circ K} = 91 \pm 7$ kcals. Brewer [28] recommends a best value of $\Delta H^\circ_{1500^\circ K} = 85 \pm 5$ kcals for the heat of the above reaction; assuming the mean heat capacity of $Al_2O(g)$ to be 12 cal. $mole^{-1}$ $deg.^{-1}$, this corresponds to $\Delta Hf^\circ_{298} = -39.4 \pm 5$ kcal. for $Al_2O(g)$, which is the value tabulated in this report. The free energy change $\Delta F^\circ_{1500^\circ K} = 28.5$ kcals [25]; hence, $\Delta S^\circ_{1500^\circ K} = 38$ eu [28]. Extrapolating the data, Brewer [28] gives $\Delta F^\circ_{2000^\circ K} = 11$ kcals and $\Delta F^\circ_{2750^\circ K} = -12$ kcals.

For the reaction $4/3\ Al(g) + 1/3\ Al_2O_3(c) = Al_2O(g)$, $\Delta F^\circ = -6000 + 9.15T \log T - 34.7\ T$ cals. $\Delta S^\circ_{1000^\circ K} = +3$ eu; $\Delta F^\circ_{1000^\circ K} = -13$ kcals; $\Delta F^\circ_{2000^\circ K} = -15$ kcals. For the reaction involving $Al_2O_3(l)$, $\Delta S^\circ_{2500^\circ K} = -4$ eu; $\Delta F^\circ_{2750^\circ K} = -13$ kcals.

The free energy of formation of $Al_2O(g)$ from the elements in their standard states is -68 kcals at 1500°K; -72 kcals at 2000°K [28].

The following table [28] gives the partial pressures (in atmospheres) of the major species in equilibrium with metal-rich alumina, or a mixture of Al and Al_2O_3:

	2000°K	2500°K	2750°K
P_{Al_2O} (atm.)	$10^{-1.2}$	$10^{0.4}$	10
P_{Al} (atm.)	$10^{-2.1}$	$10^{-0.5}$	1
P_O (atm.)	10^{-12}	10^{-8}	$10^{-6.5}$

Upon the assumption that Al_2O and Al continue to be the predominant vapor species, there is a considerable decrease in the vapor pressure of alumina as one goes from a metal-rich composition to a constant boiling composition: The following table [28] gives the calculated vapor pressure (in atmospheres) for a constant boiling composition corresponding to the passage of an inert gas over the alumina:

	2000°K	2500°K	2750°K
P_O (atm.)	$10^{-8.1}$	$10^{-4.9}$	$10^{-3.8}$
P_{Al} (atm.)	$10^{-8.3}$	$10^{-5.1}$	$10^{-4.0}$
P_{Al_2O} (atm.)	$10^{-9.4}$	$10^{-5.7}$	$10^{-4.3}$

The main problem in checking the accuracy of the above assumption experimentally is that it is extremely difficult to study the vaporization of alumina in neutral or oxidizing conditions. The importance of such species as AlO, Al_2O_2 etc. has not yet been clearly substantiated. In Brewer's experiments [25], he evaporated Al_2O_3 in a tungsten cell; however, Ackerman and Thorn contend [29] that the observed volatility was due to the reaction between alumina and tungsten. In reviewing both his own data and that of Ackerman and Thorn, Brewer [28] has commented that the observed vapor pressure of alumina cannot be accounted for solely in terms of this reaction. The observed vapor pressure of alumina, correcting to neutral conditions and assuming Al is the predominant vapor species, is four times greater than the pressure calculated according to the reaction $Al_2O_3(l) = 2Al\ (g) + 3O(g)$:

	$\Delta F°/T$ for $Al_2O_3(l) = 2Al(g) + 3O(g)$ assuming Al sole gas species (cal/deg/mole)		Al partial pressures for constant boiling alumina corrected to neutral conditions (atmospheres)	
	Observed	Calculated	Observed	Calculated
2300°K	124.	138.8	$10^{-5.4}$	$10^{-6.0}$
2450°K	107	120.3	$10^{-4.9}$	$10^{-5.3}$
2600°K	90	103.8	$10^{-4.0}$	$10^{-4.6}$

Brewer [28] believes that it is unlikely that this discrepancy can be attributed to errors in thermodynamic data or the temperature scale. He concluded that there is an important vapor species other than Al_2O or Al in the neutral vapor, unless the discrepancy arises from errors in the experimental technique. The mass-spectrometer [27] has so far failed to detect species of higher oxidation state, but a characteristic spectrum attributed to AlO is observed in arcs. The dissociation energy of AlO is not known with any certainty; Gaydon [30] gave a questionable value of 88 ± 7 kcal. in 1947. More recently, Brewer [31] has recommended D_0 = 119 ± 8 kcal. per mole, and that is the value tabulated in this report. There is some evidence for predissociation in the ground state [32] leading to a dissociation energy in the lower electronic state of 0.93 ev. This supposed predissociation is apparently excluded by recent observations of Lagerqvist [33].

As far as vaporization under reducing or near neutral conditions are concerned, Brewer sums up [28] by recommending that thermodynamic calculations be carried out on the basis of Al and Al_2O as the sole vaporizing species. This assumption leads to a maximum possible error of a factor of four.

The vapor pressure of aluminum oxide having a composition on the oxygen-rich side of its homogeneity range has not yet been undertaken. It is anticipated, however, that vapor species having higher oxidation states are likely to be of importance. An active Bureau program has as one of its projected tasks the determination of the vapor pressure using a rhenium Knudsen cell. It is hoped that this will yield data pertaining to less reducing conditions than those obtainable with molybdenum and tungsten cells.

A preliminary qualitative study using the Bureau's solar furnace has shown that the rate of vaporization of molten alumina is considerably reduced by small partial pressures of oxygen [21].

As far as investigations of the volatility of alumina in the presence of other gaseous atmospheres are concerned, only studies in the presence of water vapor appear to have been undertaken. The measurements have been made only over a limited temperature range. Up to 1600°C no effect on the rate of vaporization has been detected in atmospheres of 4-10 mm H_2O, using a microbalance technique [21]. Glemser used a transpiration method and 1 atmos. H_2O (g) without detecting significant changes in the volatility of alumina at temperatures up to 1700°C [34]. However, qualitative experiments with the solar furnace [21] indicate that the volatility of molten alumina is considerably enhanced by a pressure of 25 mm. H_2O (g).

The only known studies on the kinetics of vaporization of alumina are currently being undertaken at the Bureau [21]. This investigation is attempting to undertake measurements in vacuum and in different partial pressures of various gases. The role of impurities in determining the rate of vaporization is also being studied.

The Vaporization of Beryllium Oxide

W. A. Chupka and J. Berkowitz [35] have recently discussed their study of the vaporization of beryllium oxide and its reaction with tungsten. The composition of the vapor above beryllium oxide held in a tungsten Knudsen cell in the range 1900° - 2400°K has been determined mass spectrometrically. The vapor consists predominantly of Be and O atoms and $(BeO)_3$ and $(BeO)_4$ molecules. Smaller amounts of the following molecules were detected: O_2, BeO, $(BeO)_2$, $(BeO)_5$, $(BeO)_6$, WO_2, WO_3 and $WO_x.(BeO)_y$ where $x = 1, 2$ and $y = 1, 2, 3$. A thermodynamic treatment of the data yielded a value of 4.6 ± 0.1 ev for the dissociation energy of the BeO molecule. Heats of vaporization have been measured for the other $(BeO)_n$ molecules. The boiling point of BeO has been crudely estimated as 3850 ± 200°C, at which temperature the vapor consists mostly of $(BeO)_4$ and somewhat smaller amounts of $(BeO)_3$ and $(BeO)_5$. The atomization energies of the WO_2 and WO_3 molecules have been measured to be 13.6 ± 0.4 ev and 19.3 ± 0.4 ev respectively. The dissociation energy of the WO molecule is estimated to be about 7.2 ev. The results on the $(BeO)_n$ species are summarized in the table below. By combining the partial pressures and heats of vaporization one may obtain the entropy of vaporization. This together with entropy of the solid would give values for the entropy of each of the species at about 2200°K. The results, however, would be at least as uncertain as the percentage uncertainty in the heats. The uncertainties of the latter as estimated by the authors are sufficiently large that very little may be inferred concerning the structures of these interesting clusters.

Composition of the Vapor Above BeO(c) in a Tungsten Knudsen Cell at 2242°K, and Heats of Vaporization of $(BeO)_n$ Molecules from Variation of Partial Pressure with Temperature.

Molecule	Partial Pressure at 2242°K (10^{-6} atm)	ΔH^{vap}_{2150} (Kcal./mole of $(BeO)_n$) (corrected)	ΔH^{vap}_{0} (Kcal./mole of $(BeO)_n$)
Be	0.5000	-	-
O	0.5000	-	-
O_2	0.0200	-	-
BeO	0.0075	165.5	172.1
$(BeO)_2$	0.0008	172 ± 8	185 ± 12
$(BeO)_3$	0.1000	161 ± 6	179 ± 9
$(BeO)_4$	0.0440	177 ± 8	198 ± 12
$(BeO)_5$	0.0030	193 ± 12	217 ± 18
$(BeO)_6$	0.0001	203 ± 15	230 ± 22

Vapor Pressure and Heat of Vaporization

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CHAPTER VI

HEAT OF FORMATION AND DISSOCIATION ENERGY

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The heats of formation of the elements considered in this report are listed in table 1. In this table are shown the heats of formation in the standard states at 0°K and 298.15°K and the energy of dissociation to atoms at 0°K and 298.15°K. All values in table 1 are from Stull and Sinke [1]* except those for fluorine which are based on the correlation by Stamper and Barrow [2]. Heats of formation and dissociation energies at the same temperature for the compounds and molecular species of the elements are shown in table 2. In this table the value for a given element or compound with the smaller number of significant figures indicates the accuracy of the value. Derived quantities are shown with larger numbers of significant figures in some cases, to show differences. Values are expressed in terms of the defined calorie: 1 calorie = 4.1840 absolute joules. The various values listed for a given substance are consistent with values for $(H_{298} - H_0)$ given in Chapter II. In many cases a justification of the selected value is given in the following text. Where no justification is given the value is generally the result of a previous correlation or is the result of the work of a single author for which reference is given. All values are subject to further revision on the basis of additional information or further analysis of existing data.

Immediately following the compound by compound discussion is a brief discussion of the thermodynamic relations in the rather complex system of solid oxides and oxyhydrates of aluminum.

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*Numbers in brackets refer to references at the end of this chapter.

Table 1

Standard Heats of Formation and Dissociation Energies of the Elements

Substance	State	$\Delta Hf°$ at 0°K	$\Delta Hf°$ at 298.15°K	ΔH to gaseous atoms at 0°K	ΔH to gaseous atoms at 298.15°K
		kcal./mole	kcal./mole	kcal./mole	kcal./mole
H	g	51.621	52.090	0	0
H_2	g	0	0	103.242	104.180
O	g	58.980	59.550	0	0
O_2	g	0	0	117.960	119.100
F	g	18.357	18.860	0	0
F_2	g	0	0	36.714	37.720
Cl	g	28.540	28.942	0	0
Cl_2	g	0	0	57.080	57.884
Al	c	0	0	76.940	77.500
Al	g	76.940	77.5	0	0
Be	c	0	0	76.887	77.900
Be	g	76.887	77.9	0	0
Mg	c	0	0	35.313	35.600
Mg	g	35.313	35.6	0	0
Li	c	0	0	38.050	38.439
Li	g	38.05	38.439	0	0

Table 2. Standard Heat of Formation and Dissociation Energy of Compounds and Gaseous Metals.

Substance	State	ΔH°f at 0°K kcal/mole	ΔH°f at 298.15°K kcal/mole	ΔH to gaseous atoms at 0°K kcal/mole	ΔH to gaseous atoms at 298.15°K kcal/mole	Reference
			Aluminum Compounds			
Al_2	g	103.88		50 ± 30		
Al_2O	c					
	g		-39.4 ±5		253.95	
AlO	c		-88 ± 10		225.05	
	g	16.92	16.89	119 ±8	120.16	
Al_2O_2	g	104.16		376 ±30		
AlO_2^-	aq		-221 ±3			
Al_2O_3-α	c	-397.5	-400.4 ±0.3	728.32	734.05	
-γ	c		-384.8 ±8		718.45	
-ρ	c		-394.0 ±8		727.65	
$Al_2O_3.H_2O$-α	c		-463.4 ±8		960.78	
-β	c		-478 ±8		975.38	
$Al_2O_3.3H_2O$-α	c		-615.4 ±12		1440.24	
-β	c		-612.6 ±14		1437.44	
AlH	g	58.03	58 ± 20	70.53	71.59	[9]
AlH_3	g		23		210.77	
$Al(OH)_3$	amorph		-304 ±4		597.32	[28]
AlF	c		-102 ±10		198.36	
	g	-59.97	-60 ±10	155.27	156.36	
AlF_2	c		-184 ±10		299.22	
	g		-114 ±5		229.22	
AlF_3	c		-355.7		489.78	
	g		-270		404.08	
$AlF_3\frac{1}{2}H_2O$	c					
$AlF_3.3H_2O$	c					
AlCl	c		-50 ±10		156.44	[5]
	g	-11.34	-11.3 ±1	116.8	117.74	
$AlCl_2$	c		-80 ±10		215.38	[5]
$AlCl_3$	g		-137.7 ±1.5		302.03	
Al_2Cl_6	c		-337.14 ±.5		665.79	[51]
	g		-307.2 ±1.3		635.85	[48,51]

Continued

Table 2 (cont'd). Standard Heat of Formation and Dissociation Energy of Compounds and Gaseous Metals.

		$\Delta H°_f$		ΔH to gaseous atoms		
Substance	State	at 0°K kcal/mole	at 298.15°K kcal/mole	at 0°K kcal/mole	at 298.15°K kcal/mole	Reference
			Beryllium Compounds			
Be_2	g			16 ±10		
BeO	c		-143.1 ±4			
	g	29.87	30.44	106 ±5	107.01	
BeH	g	77.51	78.1	51 ±7	51.89	[9]
$Be(OH)_2$	c		-216.8		517.98	[28]
	g		-162.4		463.58	
BeF	g	3.24	3.80	92 ±30	92.96	
BeF_2	c		-227 ±10		342.62	
	g		-178		293.62	
BeCl	g	36.43	36.98	69 ±30	69.86	
$BeCl_2$	c		-109.2		224.98	
	g		-84		219.78	
Be_2Cl_4	g		-188		459.57	
			Magnesium Compounds			
Mg_2	g	63.43		7.2 ±2		
MgO	c		-143.7 ±2		238.85	
	g	4.29	4.19	90 ±5	90.96	
MgO[illegible]	c		-148.9		303.60	
MgF	g	-20.33	-20.44	74 ±20	74.90	
MgF_2	c		-263.5		336.82	[28]
Mg[illegible]	g	1.85	1.80	62 ±20	62.74	
MgH	g	40.93	40.83	46 ±10	46.89	[42]

Continued

Table 2 (cont'd). Standard Heat of Formation and Dissociation Energy of Compounds and Gaseous Metals.

		ΔH°_f		ΔH to gaseous atoms		
Substance	State	at 0°K kcal/mole	at 298.15°K kcal/mole	at 0°K kcal/mole	at 298.15°K kcal/mole	Reference
Lithium Compounds						
Li_2	g	50.35	50.47	25.76 ±0.10	26.41	
LiO	g	14.03		<83 ±5		
Li_2O	c	-140.91	-142.4	275.99	278.83	[28]
LiH	c		-21.64		112.17	
	g	33.66	34.27	56.01 ±10	56.90	
LiOH	c	-115.03	-116.4 ±.2	263.68	266.48	
	g					
LiF	c		-146.3		203.60	[28]
	g	-77.2	-77.2	133.6 ±4	134.5	
$(LiF)_2$	g	-218.0	-219.2	330.8	333.8	
$(LiF)_3$	g	-352.6	-355.5	521.8	527.4	
$(LiF)_4$						
LiCl	c		-97.70 ± 2		165.08	[28]
	g	-43.8	-43.8	110.4 ±4	111.2	
$(LiCl)_2$	g	-140.4	-141.2	273.6	276.0	
$(LiCl)_3$	g	-220.2	-222.1	420.0	24.2	
Li_2FCl	g	-179.2	-180.2	302.2	304.9	
LiN	c					
	g					
Li_3N	c			-47.2		[28]

Discussion of Substances in Table 2

A. Aluminum and its compounds:

1. $Al_2(g)$ $D_0 \approx 50 \pm 30$ kcal/mole or 2.2 e.v.

The dissociation energy for Al_2 is very uncertain. Sharma [4] reported spectra attributed tentatively to this molecule. If taken to apply to the ground state, a linear Birge-Sponer extrapolation gives a dissociation energy of 83 kcal/mole. An examination of the behavior of vapor pressure data suggests that a value roughly of the magnitude of 65 kcal/mole might help some in accounting for the results. As a rough interpolation between their mass spectroscopic value for Si_2 and a value for Mg_2 (see Mg reference), Drowart and Honig [3] have suggested a value of 1.7 e.v. which is about 39 kcal/mole. The value of 50 kcal/mole has been selected arbitrarily, presuming that the Birge-Sponer extrapolation may be high in view of the existence of the lower estimates.

2. $Al_2O(c)$

Gattow [5] estimated $\Delta H^\circ f_{298}$ on the basis of a Born-Haber cycle and recent literature, but his value of -25 kcal/mole must be disregarded because it leads to a negative heat of sublimation. No evidence for the existence of this solid has been presented.

3. $Al_2O(g)$ $\Delta H_f^\circ{}_{298} = -39.4 \pm 5$ kcal/mole.

For the reaction $\frac{4}{3}\,Al(l) + \frac{1}{3}\,Al_2O_3(c) = Al_2O(g)$ $\Delta H^\circ_{1500} = 85 \pm 5$ kcal./mole. This value was obtained by Brewer [6] on the basis of an analysis of the data of Porter, Schissel, and Inghram [7] and of Brewer and Searcy [8], giving greater weight to the former. This leads to a value for $\Delta H^\circ f_{298}(Al_2O) = -39.4$. Gattow [5] estimated $\Delta H^\circ f_{298} = -40$ kcal/mole on the basis of a Born-Haber cycle. See also recent work by DeMaria, Drowart and Inghram [93].

4. $AlO(c)$ $\Delta H_f^\circ{}_{298} = -88 \pm 10$ kcal/mole.

Gattow [5] estimated the heat of formation of the solid on the basis of a Born-Haber cycle and recent literature. The existence of the compound in the solid phase is not established.

5. $AlO(g)$ $D_0 = 119 \pm 8$ kcal/mole

In still accepting Brewer's estimate [5] of 119 kcal/mole, we note that this value can be obtained as an arithmetic mean between the recent value of 133.5 ± 3 kcal/mole of Veits and Gurvitch [11].

based on the coefficient of the dissociation reaction in an oxy-acetylene flame, and a value < 104 kcal/mole more recently reported by Inghram, Chupka and Berkowitz [12], based on mass spectrometer observations. The value given above is in remarkably good agreement with the recently published value of 120 kcal/mole reported by DeMaria, Drowart and Inghram [93].

6. $Al_2O_2(g)$ $D_o = 376 \pm 30$ kcal/mole

This molecule has recently been observed and ΔH_o^o for the reaction $Al_2O_2(g) = 2AlO(g)$ has been estimated to be -138 ± 15 kcal/mole by DeMaria, Drowart and Inghram [93].

7. AlO_2^-. Aluminate ion. $\Delta H^\circ f_{298} = -221 \pm 3$ kcal/mole.

Kelley, et al [13] determined the heat of solution of aluminum in potassium hydroxide(2N). The heat of formation of aluminate ion in a solution of 2N $KAlO_2$, 356.6 KOH • 9845 H_2O was calculated, using -114.7 for the heat of formation of KOH(aq 2M) and assuming the K^+ ion to be in its standard state. No corrections for hydrolysis were applied.

8. Al_2O_3-α(c). Corundum. $\Delta H^\circ f_{298} = -400.4 \pm 0.3$ kcal/mole.

There appears to be little doubt as to the value of ΔHf_{298}. The following values have been recently reported on the basis of direct combustion of highly pure aluminum in oxygen.

Snyder and Seltz (1945) [14]	-399.09 ± 0.06
Holley and Huber (1951) [15]	-400.29 ± 0.3
Schneider and Gattow (1954) [16]	-400.6 ± 2 (-402 ± 2)
Mah (1957) [17]	-400.4 ± 0.3

The only important possible error appears to be that suggested by Schneider and Gattow, that up to 0.5 per cent error may be introduced by formation of some γ - Al_2O_3 in the reaction. The value in parentheses reflects a suggested correction for this crystalline form by Schneider and Gattow. However, the possibility that any such large correction is required was largely dispelled by the work of Mah [17] who found only a small quantity of product which was not corundum. The occurrence of the undesired phase principally in the dust collected from the bomb walls suggested that this oxide might be most troublesome in regions where the gaseous products are quickly cooled. The possible effect of a large surface energy due to fineness of subdivision of the product has not been investigated directly. Information about the heat of formation of Al_2O_3 at 1120 - 1380°K may be obtained from the work of Treadwell and Terebesi [18] on the oxygen-aluminum-aluminum oxide electrode.

Further experimental work on the heat of formation of Al_2O_3-α is described in references [19-29].

9. Al_2O_3-γ (c) $\Delta H^\circ_{f298} = -384.8 \pm 8$ kcal/mole.

Kelley et at [13] determined the heats of solution of aluminum and of Al_2O_3-γ in aqueous KOH. They adjusted their solution to give the same final concentrations in each reaction, and itemized corrections for impurities and side effects. Buchner [30] carried out a similar pair of reactions in which the solvent was aqueous HF. His work leads to a value of -188.7 for $\frac{1}{2}\Delta H_f(Al_2O_3\text{-}\gamma)$ which is significantly different from the work of Kelley. Although Buchner's value for the heat of solution of Al in HF was confirmed by Wartenberg [31], the more negative value of -192.4 found by Kelley et al is more consistent with other values presented in table 2. It should be realized that aluminum forms a series of complex ions both with hydroxides and with fluorides, each of which may introduce significant heat effects.

10. Al_2O_3-ρ (c) $\Delta H^\circ_{f298} = -394.0 \pm 8$ kcal/mole.

This little known phase of alumina is formed by vacuum dehydration of alpha or beta aluminum trihydrate. Michel [33] measured the heat of dehydration at 210 - 230° and adjusted it to 25°C.

11. $Al_2O_3(g)$

The existence of this species has not been demonstrated. Wartenberg [31] has estimated the heat of sublimation to be at least 150 kcal/mole, and disagrees with the interpretation by Brewer and Searcy of the vaporization processes. The paucity of data upon which he bases his argument must cause it to be disregarded in the face of detailed mass spectrometric data obtained by other workers. DeMaria, Drowart and Inghram [93] estimate the heat of atomization to be 500 kcal/mole, a value which requires a much greater heat of vaporization than that estimated by Wartenberg.

12. Al_2O_3-H_2O-α(c) Boehmite $\Delta H^\circ_{f298} = -463.4 \pm 8$ kcal/mole.

Roth [32] determined the heat of dehydration of alpha alumina monohydrate by reaction calorimetry. His value for this process is confirmed within 0.2 kcal by a direct determination of the heat of dehydration in vacuum by Michel [34].

13. $Al_2O_3 \cdot H_2O$-β (c) Diaspore $\Delta H^\circ_{f298} = -478 \pm 8$ kcal/mole.

The data on this compound are inconsistent. The most useful piece of information for relating it to other compounds is the finding by Huttig and Wittgenstein [35] that the heat of dehydration of beta alumina monohydrate to alpha alumina is the same as the heat of dehydration of alpha alumina monohydrate to gamma alumina. Their estimate is based on measurements of the vapor pressure of water over the hydrate.

14. $Al_2O_3 \cdot 3H_2O$-α(c) Hydrargillite $\Delta H^\circ_{f298} = -615.4 \pm 12$ kcal/mole.

The heat of dehydration of alpha alumina trihydrate to alpha alumina monohydrate was determined from vapor pressure measurements by Fricke and Severin [36]. The value is consistent with a value determined from the heat of solution of alpha alumina trihydrate in aqueous sodium hydroxide directly measured by Roth, Wirths and Berendt [27]. The latter value is confirmed within 3 kcal by Russell, Edwards, and Taylor [37] who evaluated the heat of solution on the basis of a difficult experiment on the solubility equilibrium as a function of temperature.

15. $Al_2O_3 \cdot 3H_2O$-β (c) Bayerite. $\Delta H^\circ_{f_{298}} = -612.6 \pm 14$ kcal/mole.

Michel [33] found 0.75 kcal for the difference in the heat of dehydration of alpha- and beta-alumina trihydrates both yielding Al_2O_3-ρ. Fricke and Wullhorst [38] determined the heats of solution of the same compounds in aqueous HF and found a difference of 1.25 kcal. Russell, Edwards and Taylor [37] calculated the heats of solution from solubility measurements in aqueous NaOH and found a difference of 2.10 kcal. An average of 1.4 kcal was selected.

? for ½ d.s.?

16. AlH_3(g). $\Delta H^\circ_{f_{298}} = 23$ kcal/mole.

There are no available experimental data for this compound. Taking the bond energy from AlH (70 Kcal) gives $\Delta H_f = 23$ kcal.

17. $Al(OH)_3$.amorphous. $\Delta H^\circ_{f_{298}} = -304 \pm 4$ kcal/mole.

No recent work has been done on this substance which is not well defined. The value reported was found by the heat of formation of $Al(OH)_3$ precipitate by bases acting on solutions of aluminum salts, and is reported in NBS Circular 500.

18. AlF(c) $\Delta H^\circ_{f_{298}} = -102 \pm 10$ kcal/mole.

No measurements have been made on solid AlF, and the occurrence of this compound has not been demonstrated. Irmann [39] has estimated the heat of formation to be -103 kcal per mole, and Brewer et al [40] estimated it to be -102 kcal/mole.

19. AlF (g) $\Delta H^\circ_{f_{298}} = -60 \pm 10$ kcal/mole.

While a spectroscopic value of 167 kcal/mole for the dissociation energy was obtained by Barrow, Johns and Smith [41], they thought it likely that the excited state studied for this estimate had a potential maximum, so that a thermochemical value was preferable. With the heat of formation here accepted, $\Delta H_{f_{298}} = -60$ kcal/mole, the dissociation energy is taken as 155.3 kcal/mole. Gaydon [42] has used 154 kcal/mole, while 155 kcal/mole was given by Gross, Hayman, and Levi [43], with Barrow, Johns, and Smith giving 158.4 kcal/mole as their thermochemical value.

20. $AlF_2(c)$ $\Delta H^\circ_{f_{298}} = -184 \pm 10$ kcal/mole.

This substance is not known. The heat of formation is estimated by Irmann [39].

21. $AlF_2(g)$ $\Delta H^\circ_{f_{298}} = -114 \pm 5$ kcal/mole.

The substance is not known; the heat of formation is estimated by Irmann [39].

22. $AlF_3(c)$ $\Delta H_{f_{298.16}} = -355.7$ kcal/mole

This value, determined by Gross, Hayman and Levi [43] is the only direct experimental determination and is based on the reaction of Al with PbF_2 in a dry state. Brewer et al [40] derived a value of -323 ± 5 on the basis of heat of hydration and heat of solution estimates. In NBS Circular 500 is reported a value of -311 obtained by a similar method of estimation, using different solution data. Work with hydrates and solutions is indicated to be very difficult by the work of Ehret and Frere [42] who found in some cases up to a year required for achievement of equilibrium, and therefore the direct dry heat determination by Gross, Hayman and Levi is preferred.

23. $AlF_3(g)$ $\Delta H^\circ_{f_{298}} = -270$ kcal/mole.

The heat of sublimation is obtained from NBS Circular 500 to be 77 kcal at 1500°K. An estimated correction to 298°K is made giving $\Delta H_{subl_{298}} = 85$ kcal/mole and a heat of formation of $AlF_3(g)$ of -270 kcal/mole.

24. $AlCl(g)$ $D_0 = 116.8$ kcal/mole or 5.06 e.v.

A thermochemical value by Gross, Campbell, Kent, and Levi [44] $\Delta H_{f_{298}} = -11.3$ kcal/mole, is accepted for AlCl, giving $D_0 = 116.8$ kcal/mole. For AlCl, as for AlF, the value obtained for D_0 is considerably above the result of a linear Birge-Sponer extrapolation, a situation typical for strongly ionic bonding.

25. $AlCl_3(g)$ $\Delta H^\circ_{f_{298}} = -137.7 \pm 1.5$ kcal/mole.

This value is from data on $Al_2Cl_6(c)$ and ΔH_{vap} from Dunne and Gregory [48], Smits and Maijering [49], and Fischer and Rohlfs [50].

26. $Al_2Cl_6(c)$ $\Delta H^\circ_{f_{298}} = -337.14 \pm 0.5$ kcal/mole.

This is obtained from heat of solution data of Coughlin [51].

27. $Al_2Cl_6(g)$ $\Delta H^\circ f_{298}$ = -307.2 ± 1.3 kcal/mole.

Δ H vaporization is from Dunne and Gregory [48].

B. Beryllium and its compounds:

1. $Be_2(g)$ D_o = 16 ± 10 kcal/mole

For Be_2, Drowart and Honig [3] have estimated that D_o is about 0.7e.v., based on a graphical interpolation between elements for which literature values exist. It would seem that such an estimate must be very uncertain.

2. BeO(c) $\Delta H^\circ f_{298}$ = -143.1 ± 4 kcal/mole.

A determination by Cosgrove and Snyder [52] gave a value ΔH_f(BeO)= -143.1 ± 0.1. The small standard deviation will probably cause this value to be generally accepted. The principal criticism which can be made of this work is the failure to determine the completeness of reaction. In a heterogeneous system of refractory materials incomplete combustion is sometimes a serious problem (viz. boron oxides). It should be noted that the two most recent determinations for ΔH_f°(BeO);-147.3 ± 0.6 (Roth, Borger, and Siemonsen [53]), and -143.1 ± 0.1, differ from one another by considerably more than the uncertainty estimated by the authors, a fact which suggests systematic errors in one or both experiments.

3. BeO(g) D_o = 106 ± 5 kcal/mole.

A dissociation energy of 106 kcal/mole has been accepted for the present report based on mass spectrometric studies of Chupka and Berkowitz [54] showing vapor species including oxide polymers. See Chapter V of this report. Some thermochemical data had appeared earlier to indicate a value near the 124 kcal/mole accepted by Gaydon [42]. It appears that the uncertainty of the value accepted could well be increased to 5 kcal/mole to take account of the possible correctness of 111 kcal/mole or 4.82 e.v. obtained spectroscopically by Lagerqvist [55].

4. $Be(OH)_2(g)$ $\Delta H^\circ f_{298}$ = -162.4 kcal/mole.

Using the heat of formation of $Be(OH)_2(c)$ from NBS Circular 500, and vaporization data of Grosswein and Seifert [56] including their interpretation of the data, the heat of formation of $Be(OH)_2(g)$ is -162.4 kcal/mole.

5. BeF (g) $D_0 = 92 \pm 30$ kcal/mole

For BeF and BeCl, two opposing effects are thought to occur relevant to the magnitude obtained by a linear Birge-Sponer extrapolation. On the one hand, the bond is partially ionic so the true value might be expected to be above the extrapolated value. On the other hand, one of the atoms (Be) has a $^1S_0$ ground state, in which case an opposite deviation is found. The view might be taken that either effect might be the larger so that the simple extrapolated value should be used as listed by Herzberg [9], with a large uncertainty. Gaydon [42] gives values indicating that he considers the reducing effect to be the larger. A comparison of heats of formation for an extensive group of fluorine compounds has led to a preference for Gaydon's value for BeF, viz., $D_0 = 92 \pm 30$ kcal/mole. His indicated uncertainties are increased somewhat in the present listing.

6. $BeF_2(c)$ $\Delta H^\circ_{f_{298}} = -227 \pm 10$ kcal/mole.

Values for $\Delta H_f(BeF_2)$ are based on a long series of reactions, which do not include a measurement of the heat of solution. An estimate was made by Brewer et al [40] leading to a value for the heat of formation of -227.0 ± 10 kcal/mole.

7. $BeF_2(g)$ $\Delta H^\circ_{f_{298}} = -178$ kcal/mole.

Sense, Snyder, and Clegg [57] have measured the heat of vaporization of $BeF_2(g)$ to 1000°C. See also Sense and Stone [58]. With the heat of formation of solid BeF_2, 3kcal for reduction to 298°K and an estimated heat of melting of 6 kcal, this leads to $\Delta H_f = -178$ kcal/mole.

8. BeCl(g) $D^\circ_0 = 69 \pm 30$ kcal/mole.

See BeF.

9. $BeCl_2(c)$ $\Delta H^\circ_{f_{298}} = -109.2 \pm 5$ kcal/mole.

The most direct and probably best determination of the heat of formation is by Siemonsen, Z. Elektrochem. 55, 327 (1951).

10. $BeCl_2(g)$ $\Delta H^\circ_{f_{298}} = -84$ kcal/mole.

Using Siemonsen's [59] value for the heat of formation of $BeCl_2(c)$ and sublimation data from NBS Circular 500, the heat of formation of $BeCl_2(g)$ is found to be -84 kcal/mole.

11. Be_2Cl_4(g) ΔH_f = -188 kcal/mole

Using the heat of sublimation of the dimer from NBS Circular 500 and the heat of formation of $BeCl_2$(c) from Siemonsen [59], the heat of formation of the dimer is calculated to be -188 kcal/mole.

C. Magnesium and its compounds

1. Mg_2(g) D_o = 7.2 kcal/mole or 0.31 e.v.

The dissociation energy for Mg_2 has been reported as estimated from the band spectrum as 0.31 e.v. or 7.2 kcal/mole by Soulen, Sthapitanonda, and Margrave (1955) [60] and also so reported by Margrave (1957) [61]. It had also been reported as 0.30 e.v. by Hamada (1931) [62] from the interval between the vapor resonance line and its short wave cut-off.

2. MgO(c) $\Delta H^\circ_{f_{298}}$ = -143.7 ±2 kcal/mole.

The most recent value for $\Delta H_{f(298)}$(MgO) is -143.7 ± 0.12 kcal/mole determined by direct combustion by Holley and Huber [15]. It is in good agreement with a previous value (143.84) which Shomate and Huffman [63] obtained from the heat of solution in HCl, but differs significantly from -146.1 ± 0.3 found previously in Moose and Parr [23] by direct combustion.

3. MgO (g) D_o = 90 kcal/mole or 3.9 e.v.

The dissociation energy for MgO is taken as 90 kcal/mole, reported as an upper limit for D_o by Porter, Chupka, and Inghram [64] on the basis of observations on electron bombarded vapor. On the basis of flame studies, Huldt and Lagerqvist [65] had proposed 120 kcal/mole and Veits and Gurvich [66] more recently have obtained 100 kcal/mole. Brewer and Porter [67] had obtained 109 kcal/mole on the basis of vapor pressure and spectroscopic measurement. A spectroscopic value of 85 kcal/mole was reported earlier by Lagerqvist and Uhler [68], based on visible band systems, but is presumed to be irrelevant if the proposal is correct that the ground state for the molecule is not the observed $^1\Sigma$ state but an unobserved $^3\Sigma$ state. The question of the ground state was mentioned by Brewer [69] and by Porter [70] and by Brewer and Porter [67]. Gaydon [42] has suggested that a triplet state may have been observed by Barrow and Crawford [71].

4. MgO_2(c) $\Delta H^\circ_{f_{298}}$ = -148.9 kcal/mole.

Only one value has been reported for the heat of formation ΔH_f = -148.9 by Blumenthal [72].

5. MgF(g) $D_0^o = 74 \pm 20$ kcal/mole.

The MgF molecule is thought to bear a resemblance to BeF in combining opposing effects related to deviations from the linear Birge-Sponer extrapolation. Similarly, MgCl bears a resemblance to BeCl. Gaydon's [42] values have been accepted for this report. Thus we have $D_0^o = 74 \pm 20$ kcal/mole for MgF and 62 ± 20 kcal/mole for MgCl.

6. MgCl(g) $D_0^o = 62 \pm 20$ kcal/mole.

See MgF.

D. Lithium and its compounds

1. Li_2(g) $\Delta H^\circ_{f_{298}} = 50.47$ kcal/mole.

Spectroscopic and vapor pressure data were reviewed by Evans, Jacobson, Munson, and Wagman [73]. While the present report involves slightly modified basic tables for solid and vapor, including isotope shift for the spectroscopic constants, the previous results for $\Delta H_{f_{298}}$ for Li_2 would apparently not be affected to the number of figures reported and are hence retained.

2. LiO (g) $D_o \leqslant 83 \pm 5$ kcal/mole.

A limiting value for D_o(LiO) of 83 kcal/mole has been reported by Blue, Berkowitz and Chupka [74] based on a mass spectrometric study of the sublimation of lithium oxide.

3. LiH(c) $\Delta H^\circ_{f_{298}} = -21.64$ kcal/mole.

The heat of formation has been determined by measurement of the heat of solution of Li(c) and LiH(c) by Gunn and Green [75] and Messer, Fasolino and Thalmayer [76].

4. LiH(g) $D_o = 56.01 \pm 10$ kcal/mole.

The dissociation energy $D_0^o = 56.01$ kcal/mole obtained by Velasco [77] from spectroscopic data is accepted as the best value at present.

5. LiOH(c) $\Delta H^\circ_{f_{298}} = -116.4 \pm 0.2$ kcal/mole.

The heat of formation is obtained using data of Gregory and Mohr [78] on the decomposition pressure. Fair agreement as to heats is obtained using data of Ditmars and Johnston [79] although there is disagreement as to the magnitude of the pressure.

See to Form
(B&R)

6. LiF(g) $D_o = 133.6 \pm 4$ kcal/mole.

For the reaction LiF(c) = LiF(g), Pugh and Barrow [80] give $\Delta H_{1060} = 62.7$ kcal/mole and Porter and Schoonmaker [81] give as an average value $\Delta H_{1073} = 64.6$ kcal/mole. Taking the mean and assuming that ΔHf°_{298} of LiF(c) is -146.3 kcal/mole. [28], a thermochemical cycle gives for D_o of LiF(g) 136.2 kcal. Theoretical calculation from an ionic model which gave excellent agreement with thermochemical values for ten other alkali halide diatomic molecules gave for LiF(g) $D_o = 131.0$ kcal/mole. From photochemical dissociation Desai [82] calculated $D_o = 132.4$ kcal/mole. The mean of the first two values is taken: $D_o = 133.6 \pm 4$ kcal/mole.

7. $(LiF)_2(g)$ $D_o = 330.8$ kcal/mole.

For the reaction $(LiF)_2(g) = 2LiF(g)$ Pugh and Barrow [80] calculated from their vapor-pressure data $\Delta E_{1060} = 53$ kcal.; this is equivalent to $\Delta H_{1060} = 55.1$ kcal. This value depends to some extent on their assumption of a value below 100 cm^{-1} for one vibrational fundamental of the dimer. For the same reaction Porter and Schoonmaker [81] recommended $\Delta H_{1073} = 64.1 \pm 3$ kcal. on the basis of their mass spectrometric free energies and a dimer entropy calculated by the method of Bauer, Diner, and Porter [83]. The latter value is tentatively adopted ($\Delta H_{1073} = 64.1 \pm 9$ kcal.), as it seems to lead to a dimerization energy more in line with an extrapolation of more accurately known values for several other alkali halides; but the uncertainty should probably be regarded as considerable.

8. $(LiF)_3(g)$ $D_o = 521.8$ kcal/mole.

Porter and Schoonmaker [81] and Berkowitz and Chupka [84] have reported ion intensities attributed to $(LiF)_3$. Though the temperatures and total pressures are not clearly defined, it seems logical to apply their data to the isomolecular reaction $2(LiF)_2(g) = LiF(g) + (LiF)_3(g)$, which would be expected to be relatively independent of temperature, total pressure, and ionization cross-sections. The two investigations correspond to equilibrium constants for this reaction (calculated to be 0.03 ± 0.01 at 1000°K) which differ by a factor of 2. The temperature dependence reported by Porter and Schoonmaker is subject to a very large percentage uncertainty, but seems to correspond on the average to $\Delta H = 3$ kcal., which is consistent with their estimate of $50 \text{ kcal} < H_{1073} < 65$ kcal. for the reaction $(LiF)_3(g) = (LiF)_2(g) + LiF(g)$. The tabulated dissociation energy of $(LiF)_3(g)$ is based on the assumption that for this reaction $\Delta H_{1073} = 58 \pm 8$ kcal.

9. $(LiF)_4(g)$

Berkowitz and Chupka [84] report a very low ion intensity attributed to this molecule. This result seems surprising in view of the relative stability which this molecule might be expected to have in a cubic configuration, not to mention other configurations which may also be important in a comprehensive statistical treatment [85]. Apparently no heat of dissociation of this molecule has been estimated, and none is recommended here.

10. LiCl(c) $\Delta H^\circ f_{298}$ = -97.70 ± 2 kcal/mole.

A recent measurement by Siemonsen and Siemonsen [88] by direct combination of the elements is in disagreement by about 3 kcal with measurements in aqueous solution [28]. Because of the weight of evidence for the latter, no change is recommended until the reason for the difference is clarified.

11. LiCl(g) D_o = 110.4 ± 4 kcal/mole.

The dissociation energy assumed was calculated to be D_o = 110.4 ± 4 kcal/mole, using the same type of thermochemical cycle as for LiF(g). In this calculation the apparent "Second-Law" heat of evaporation of LiCl(l) [28, p. 792] was increased by 4.2 kcal/mole to correct for the presence of dimer and trimer in the vapor according to the results of Miller and Kusch [86,87]; in addition, ΔHf°_{298} of LiCl(c), was assumed to be the average of the two values -97.70 kcal/mole [28, p. 433] resulting from a thermochemical cycle and -94.8 kcal/mole found [88] by direct combination of the elements. From the photochemical absorption limit Desai [82] obtained D_o = 118.0 kcal/mole, but the thermochemical value is considered to be more reliable because the thermal data are precise.

12. $(LiCl)_2(g)$, $(LiCl)_3(g)$ D_o = 273.6, 420.0 kcal/mole.

From an analysis of their molecular-beam data at a total pressure of 10^{-2}mm Miller and Kusch [86] reported for the two reactions $(LiCl)_2(g) = 2LiCl(g)$ and $(LiCl)_3(g) = (LiCl)_2(g) + LiCl(g)$ the respective values ΔE_{870} = 51.1 ± 0.3 kcal. and ΔE_{870} = 34.2 ± 1.8 kcal. They calculated also the equilibrium constants for these reactions; under these conditions they found lithium chloride vapor to contain more dimer than monomer, and a few per cent of trimer. Their detection was subject to more uncertainty than in the case of alkali halides other than lithium salts, and their statements of precision have been criticized as being much too small indications of the true uncertainty by Bauer, Diner, and Porter [83], who however arrived at a value of ΔE for the first reaction above which differs fortuitously by only 0.2 kcal. Miller and Küsch's values have been assumed.

13. $Li_2FCl(g)$ D_o = 302.2 kcal/mole.

It appears that no evidence of the existence of this molecule has been reported, but its importance can be predicted on theoretical grounds. It may be noted that for the reaction $(LiF)_2(g) + (NaF)_2 = 2NaLiF_2$, in which a somewhat analogous molecule is formed, Porter and Schoonmaker [81] found approximately $\Delta S^\circ = 4$ eu and $\Delta H^\circ = -0.2$ kcal., which compare favorably with the respective values Rln 4 and zero roughly predicted from symmetry considerations. The tabulated dissociation energy of $Li_2FCl(g)$ is based on the assumption that for the reaction $(LiF)_2(g) + (LiCl)_2(g) = 2\ Li_2FCl(g)$, $\Delta H_o = 0$.

A Brief Review of the Heat Relationships Among the Crystalline Oxides and Oxyhydrates of Aluminum

The principal solid oxide of aluminum is Al_2O_3. Lower crystalline oxides have been proposed and some calculations made concerning their stability, but no experimental heat measurements involving them have been made. Examination of the reported crystalline forms of aluminum trioxides (alumina) and the formulas and crystalline forms of hydrated alumina indicate that the phase behavior of the aluminum-oxygen-water system is only very imperfectly known. For example Russell, et al [89] list the properties of nine crystalline forms of Al_2O_3 and name two other forms that have been reported. In addition to an amorphous precipitated hydroxide of indefinite composition there are a monohydrate and a trihydrate, each of which exhibits two well known crystalline forms. A third crystalline form has been reported for the monohydrate, and there are a number of transition hydrates. The phase relations in this group of compounds have not been clearly defined and most of the phases of alumina named are not shown on any published phase diagram.

Accurate heat measurements on Al_2O_3 have been limited to α and γ phases. The exact identities and thermal stabilities of the other phases of Al_2O_3 appear not to have been established except for an indication by Michel [33] of certain heats of dehydration leading to the ρ phase. Some of these phases, such as that called X-phase by Schneider and Gattow [16] may be important. For instance the latter appears to form when the aluminum combustion products are quickly cooled on the basis of its location when found in bomb calorimetric experiments. There is a considerable body of literature dealing with the heats of dehydration and hydration involving the mono-and tri-hydrates and certain transition hydrates. While the data may be of value in estimating relative stabilities, it does not appear to be sufficiently definitive to allow accurate assignments of heats of formation in all cases. See References [89,90] for a discussion of thermal processes observed in the hydrates. There follows a summary of experimental heat measurements which have been made on the interrelationships of members of this group of compounds. The numerous measurements are by no means internally consistent. This discussion provides the basis for the selection of values for the heats of formation in Table 2 for these compounds and for the brief previous discussion of each compound listed.

Summary of sources of information on aluminum oxides and oxyhydrates.

1. Buchner [30] measured the heat of solution of aluminum and of Al_2O_3-γ in 20% aqueous HF.
   a. $Al + 3HF\text{(20\% aq.)} = AlF_3\text{(aq)} + 3/2\ H_2\text{(g)}$ $\Delta H = -\ 123.9$ kcal/mole.
   b. $\frac{1}{2}Al_2O_3\text{-}\gamma + 3HF\text{(20\% aq)} = AlF_3\text{(aq)} + 3/2\ H_2O$ $\Delta H = -\ 37.8$

2. Wartenberg [31] confirmed Buchner's value for reaction 1.a. (above)
   $Al + 3\ HF\ \text{(12\% aq)} = AlF_3\ \text{aq} + 3/2\ H_2\text{(g)}$ $\Delta H = -\ 124.4 \pm 1$

3. Kelley et al [13] determined the heats of solution of aluminum and of Al_2O_3-γ in aqueous KOH.
   a. $Al + KOH\text{(aq 2M)} + H_2O\text{(l)} = K^+ + AlO_2^-\text{(aq)} + 3/2\ H_2\text{(g)}$ $\Delta H = -\ 98.010 \pm 0.126$
   b. $Al_2O_3\text{-}\gamma + KOH\text{(aq 2M)} = K^+ + AlO_2^-\ \text{(aq)} + \frac{1}{2}\ H_2O\text{(l)}$ $\Delta H = -8.064 \pm 0.500$

4. Fricke and Wullhorst (and Wagner)[38] determined the heat of solution of alpha alumina trihydrate and of beta alumina trihydrate in aqueous HF.
   a. $\frac{1}{2}\ Al_2O_3.3H_2O\text{-}\alpha + 3\ HF\ \text{(12\% aq)} = AlF_3\text{(aq)} + 3H_2O\text{(l)}$ $\Delta H = -\ 36.59 \pm 0.2$
   b. $\frac{1}{2}\ Al_2O_3.3H_2O\text{-}\beta + 3HF\text{(12\% aq)} = AlF_3\text{(aq)} + 3H_2O\text{(l)}$ $\Delta H = -37.84 \pm 0.3$

5. Fricke and Severin [36], from water vapor pressure measurements, determined the heat of transition of böhmite to bayerite and hydrargillite
   a. $\frac{1}{2}Al_2O_3.H_2O\text{-}\alpha + H_2O\text{(g)} = \frac{1}{2}\ Al_2O_3.3H_2O\text{-}\beta$ $\Delta H = -\ 16.2$ kcal.
   b. $\frac{1}{2}Al_2O_3.H_2O\text{-}\alpha + H_2O\text{(g)} = \frac{1}{2}\ Al_2O_3.3H_2O\text{-}\alpha$ $\Delta H = -\ 18.15$ kcal

6. Roth, Wirths and Berendt [27] determined the heat of solution of alpha alumina trihydrate in aqueous sodium hydroxide. We adjusted the value to 298.15°K.
   $\frac{1}{2}Al_2O_3.3H_2O\text{-}\alpha + NaOH\text{(400 g. 30\%)} = Na^+ + AlO_2^- + 2H_2O$ $\Delta H = 3.95$

7. Roth [32] determined the heat of transition of three samples of hydrated γ-Al_2O_3 to α-Al_2O_3 by heating through the transition in a bomb, and by adjusting for the composition of the starting materials derived:
   a. $\frac{1}{2}Al_2O_3\text{-}\gamma = \frac{1}{2}Al_2O_3\text{-}\alpha$ $\Delta H = -\ 3.9$ kcal/mole.
   b. $\frac{1}{2}Al_2O_3.H_2O\text{-}\alpha = \frac{1}{2}Al_2O_3\text{-}\alpha + \frac{1}{2}H_2O\text{(l)}$ $\Delta H = 1.2$
   c. $\frac{1}{2}Al_2O_3.3H_2O\text{-}\alpha = \frac{1}{2}Al_2O_3\text{-}\alpha + 3/2\ H_2O\text{(l)}$ $\Delta H = 5.65$
   and further derived
   d. $\frac{1}{2}Al_2O_3.H_2O\text{-}\alpha = \frac{1}{2}Al_2O_3\text{-}\gamma + \frac{1}{2}H_2O\text{(l)}$ $\Delta H = +\ 5.15$
   e. $\frac{1}{2}Al_2O_3.3H_2O\text{-}\alpha = \frac{1}{2}Al_2O_3\text{-}\gamma + 3/2\ H_2O\text{(l)}$ $\Delta H = +\ 9.6$

8. Russell, Edwards and Taylor [37] determined the solubility equilibria in sodium hydroxide solutions of the alpha monohydrate and alpha and beta trihydrates of alumina. From these equilibria he calculated heats of solution.
   a. $\frac{1}{2}Al_2O_3.H_2O\text{-}\alpha + NaOH\text{(aq}\ \infty\text{)} = Na^+ + AlO_2^-\text{(aq. sat)} + H_2O\text{(l)}$ $\Delta H = 4.76$

b. $\frac{1}{2}Al_2O_3.3H_2O-\alpha + NaOH(aq, \infty) = Na^+ + AlO_2^-(aq, sat.) + 2H_2O(l)$
$\Delta H = 7.34$

c. $\frac{1}{2}Al_2O_3.3H_2O-\beta + NaOH(aq, \infty) = Na^+ + AlO_2^-(aq, sat.) + 2H_2O(l)$
$\Delta H = 5.24$

9. Huttig and Wittgenstein [35] determined the vapor pressures of water during the dehydration of alpha and beta monohydrate and the stepwise dehydration of alpha trihydrate of alumina. From their vapor pressure equations they derived the heats of reaction.
a. $\frac{1}{2}Al_2O_3.H_2O-\alpha = \frac{1}{2}Al_2O_3-\gamma + \frac{1}{2}H_2O(g)$ $\Delta H = 15.9$ kcal.
b. $\frac{1}{2}Al_2O_3.H_2O-\beta = \frac{1}{2}Al_2O_3-\alpha + \frac{1}{2}H_2O(g)$ $\Delta H = 15.9$ kcal.
c. $\frac{1}{2}Al_2O_3.3H_2O-\alpha = \frac{1}{2}Al_2O_3.H_2O-\beta + H_2O9g)$ $\Delta H = 21.57$ kcal.
d. $\frac{1}{2}Al_2O_3.H_2O-\beta = \frac{1}{2}Al_2O_3-\gamma + \frac{1}{2}H_2O(g)$ $\Delta H = 14.25$ kcal.

10. Michel [33] calorimetrically studied the dehydration of alpha and beta alumina trihydrates in vacuum and determined the heat of dehydration to form rho phase alumina. Values were adjusted from 210 - 230°C to 25°C.
a. $\frac{1}{2}Al_2O_3.3H_2O-\alpha = \frac{1}{2}Al_2O_3(\rho) + 3/2\ H_2O(g)$ $\Delta H = 24$ kcal.
b. $\frac{1}{2}Al_2O_3.3H_2O-\beta = \frac{1}{2}Al_2O_3(\rho) + 3/2\ H_2O(g)$ $\Delta H = 23.25$

11. Michel [34] calorimetrically studied the dehydration of alpha alumina monohydrate in vacuum to form gamma alumina. Measurements made at 500°C were adjusted to 25°C.
$\frac{1}{2}Al_2O_3.H_2O-\alpha = \frac{1}{2}Al_2O_3-\gamma + \frac{1}{2}H_2O(g)$ $\Delta H = 10.2$ kcal

12. Klever [37} gives the heat of solution of bayerite in aqueous HF as functions of temperature and concentration.

13. See NBS Circular 500 for references to the work of Bau i, Berthelot and Thomsen, leading to a value for the heat of formation of $Al(OH)_3$ precipitate.

The reactions given above lead to thermal relationships between the various species of aluminum compounds as listed in Table 3, below. These relationships are intended to reveal consistencies and inconsistencies in the findings of the various workers and therefore obviously do not themselves form a consistent set of relationships. By their use several quantities were selected on the basis of the type and manner of conduct of the experiments and the consistency with other related quantities, to represent the best values. Individual measurements rather than averages were generally selected. In deriving the relationships shown the required heats of formation for $H_2O(g)$, $H_2O(l)$ and for several substances in solution were taken from NBS Circular 500.

Figure 1 shows the energy states of the aluminum compounds. In this figure is shown a closed cycle involving Al, $Al_2O_3-\gamma$, $Al_2O_3.H_2O-\alpha$, $Al_2O_3.3H_2O-\alpha$, AlO_2^- which is internally consistent and which provides strong evidence for the validity of the values selected for these compounds. Each transition required is based closely on original data without significant adjustment.

ENERGY LEVELS IN THE ALUMINUM-OXYGEN-OXYHYDRATE SYSTEM

Energy values and differences are given in kilocalories per mole.

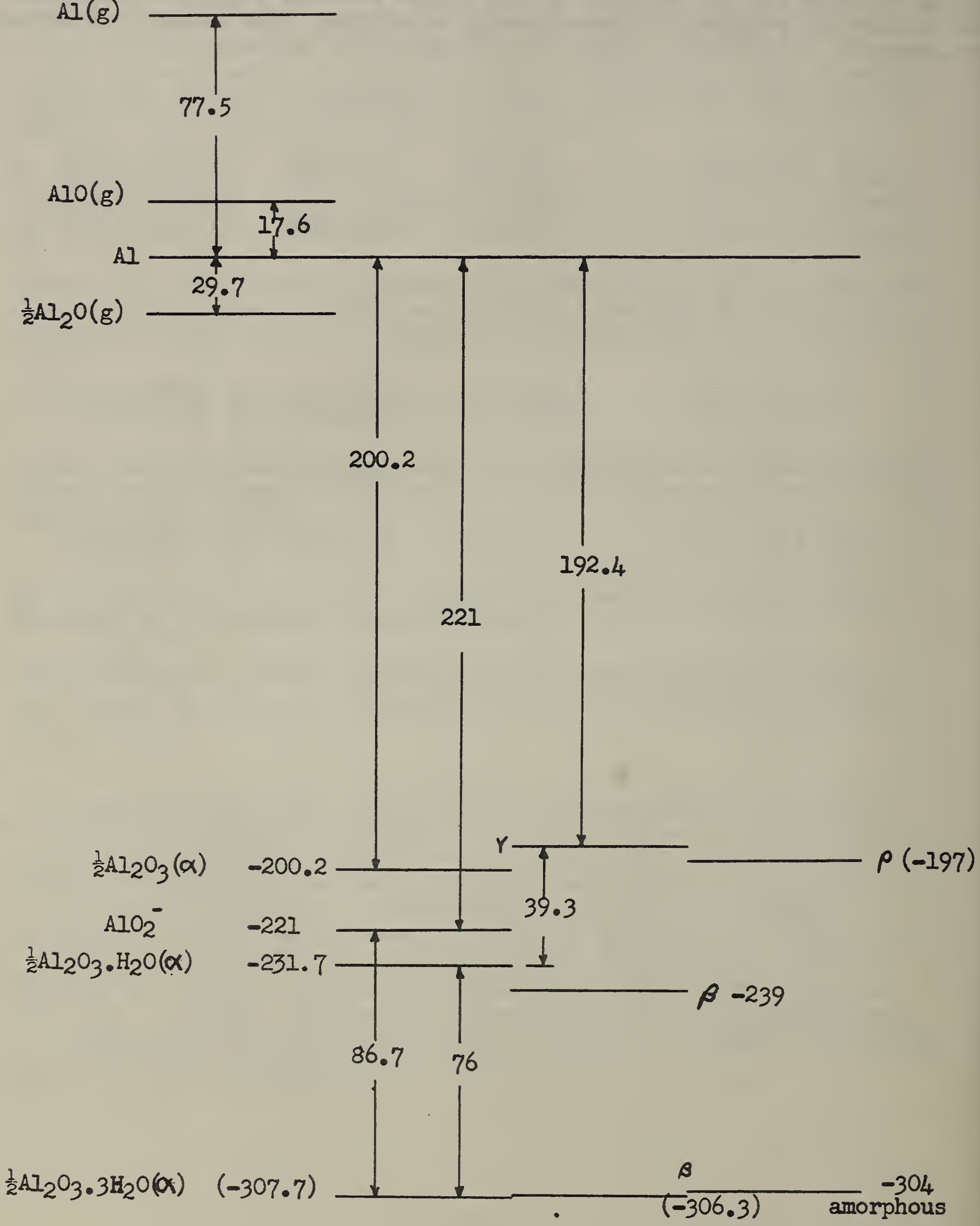

Figure 1

Table 3. Observed Thermal Relationships in Crystalline Aluminum - Oxide - Oxyhydrate System

(Because derived from conflicting observed data the relationships below are not internally consistent and are for discussion only).

Equation	Source(a)		Method
1	see p. 63	$\Delta H_f(\frac{1}{2}Al_2O_3-\alpha) = -200.2$ (selected)	direct combustion
2	1,2	$\Delta H_f(\frac{1}{2}Al_2O_3-\gamma) = -188.7$	HF solution heat
3	3	$\Delta H_f(\frac{1}{2}Al_2O_3-\gamma) = -192.4$ (selected)	KOH solution heat
4	4,2	$\Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\alpha) = -292.75$	HF solution heat
5	3	$\Delta H_f(AlO_2^-) = -221.0$	KOH solution heat
6	6	$\Delta H_f(AlO_2^-) = \Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\alpha) + 86.76$ (86.70 selected)	NaOH solution heat
7	8	$\Delta H_f(AlO_2^-) = \Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\alpha) + 89.02$	NaOH solubility vs temp.
8	4	$\Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\beta) = \Delta H\ \frac{1}{2}(Al_2O_3.3H_2O-\alpha) + 1.25 \pm 0.5$	HF solution heat
9	8	$\Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\beta) = \Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\alpha) + 2.10$	NaOH solubility vs temp.
10	10	$\Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\beta) = \Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\alpha) = +0.75 \pm 0.25$	direct heat of dehydration.
11	7(b)	$\Delta H_f(\frac{1}{2}Al_2O_3-\gamma) = \Delta H_f(\frac{1}{2}Al_2O_3.H_2O-\alpha) + 39.29$ (39.3 selected)	HCl•HF solution heat
12	11	$\Delta H_f(\frac{1}{2}Al_2O_3-\gamma) = \Delta H_f(\frac{1}{2}Al_2O_3.H_2O-\alpha) + 39.1$	direct heat of dehydration
13	8	$\Delta H_f(AlO_2^-) = \Delta H_f(\frac{1}{2}Al_2O_3.H_2O-\alpha) + 18.21$	NaOH solubility vs temp.
14	5	$\Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\beta) = \Delta H_f(\frac{1}{2}Al_2O_3.H_2O-\alpha) -74.0$	H_2O vapor pressure
15	5	$\Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\alpha) = \Delta H_f(\frac{1}{2}Al_2O_3.H_2O-\alpha) + 75.95$ (selected)	H_2O vapor pressure
16	9	$\Delta H_f(\frac{1}{2}Al_2O_3.H_2O-\beta) = \Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\alpha) + 79.37$	H_2O vapor pressure
17	9	$\Delta H_f(\frac{1}{2}Al_2O_3-\gamma) = \Delta H_f(\frac{1}{2}Al_2O_3.H_2O-\beta) + 43.15$	H_2O vapor pressure
18	9	$\Delta H_f(\frac{1}{2}Al_2O_3.H_2O-\beta) = \Delta H_f(\frac{1}{2}Al_2O_3-\alpha) -44.8$	H_2O vapor pressure
19	9	$\Delta H_f(\frac{1}{2}Al_2O_3.H_2O-\alpha) = \Delta H_f(\frac{1}{2}Al_2O_3-\gamma) - 44.8$	H_2O vapor pressure
20	7	$\Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\alpha) = \Delta H_f(\frac{1}{2}Al_2O_3-\gamma) - 112.08$	HF solution
21	7	$\Delta H_f(\frac{1}{2}Al_2O_3.3H_2O-\alpha) = \Delta H_f(\frac{1}{2}Al_2O_3-\alpha) - 108.13$	Heat of transition in bomb

Table 3 (cont'd). Observed Thermal Relationships in Crystalline Aluminum - Oxide - Oxyhydrate System

Equation	Source(a) Ref.		Method
22	7(b)	$\Delta H_f(\frac{1}{2}Al_2O_3 \cdot H_2O\text{-}\alpha) = \Delta H_f(\frac{1}{2}Al_2O_3\text{-}\gamma)$ -39.2	Heat of transition in bomb
23	10	$\Delta H_f(\frac{1}{2}Al_2O_3\text{-}\rho) = \Delta H_f(\frac{1}{2}Al_2O_3 \cdot 3H_2O\text{-}\alpha)$ $+110.7$ (selected)	Direct heat of dehydration

(a) Unless otherwise indicated source refers to the summary list of sources immediately preceeding.

(b) Because of the method of performing the experiment, reaction 7d, the sum of reactions 7a and 7b, is considered to be at least as accurate as if not more accurate than either 7a or 7b separately, and can be used, despite the inconsistency of the heat value of 7a with that adopted in this report for the difference between Al_2O_3-α and Al_2O_3-γ.

Heat of Formation and Dissociation Energy

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CHAPTER VII

PREPARATION AND PURIFICATION

by

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I. Oxides and Hydroxides

A. Alumina and Its Hydrates

The origin of the names of the aluminas is diverse. Some of the original names have been discarded and new ones added as new phases have been identified or suspected. Table 1, taken from the report of Russell *et al.* [1], gives the best established nomenclature for the aluminas. Several of these are still disputed. The properties of some of the aluminas are given in table 2, taken from Ervin and Osborne [2]. The dehydration and hydration processes shown in table 3 are taken from Tertian and Papée [3]. This table shows a rho (ρ) form, not listed in tables 1 or 2, which results from the low pressure dehydration of gibbsite and bayerite.

The methods of preparation are numerous. However, most of them involve the dehydration or hydration of one of the aluminas or their hydrates. Procedures for preparing the aluminas listed in table 1 are discussed, with the exception of *kappa* alumina.

Table 1

Nomenclature of the Aluminas

Alcoa[1][4][5]	Mineralogical	Haber[6]	Weiser and Millikan[7]	Other
Alpha Alumina Trihydrate	Gibbsite or Hydrargillite	Gamma Series	Gamma Alumina Trihydrate	Aluminum Hydroxide Orthoaluminic acid
Beta Alumina Trihydrate	Bayerite	Gamma Series	Alpha Alumina Trihydrate	Aluminum Hydroxide Bauxite Dihydrate[8]
Alpha Alumina Monohydrate	Boehmite	Gamma Series	Gamma Alumina Monohydrate	Aluminum Hydroxide Bauxite[9]
Beta Alumina Monohydrate	Diaspore	Alpha Series	Alpha Alumina Monohydrate	Meta-aluminic Acid
Alpha Alumina	Corundum	Alpha Series	Alpha Alumina	

Dehydrated Aluminas

Alcoa[1][4][5]	Rooksby[10]
Gamma	Delta and Gamma
Delta	Delta and Theta
Eta	Gamma
Theta	Theta
Kappa	Kappa and Theta
Chi	Chi and Gamma

Table 2

Properties of the Compounds

Name	Composition	Crystal System	Refractive Index	Optic Sign	Density g/cc	Hardness Moh	Source of Data
Corundum (Alpha-alumina)	Al_2O_3	Hexagonal	$\varepsilon=1.760$[a] $\omega=1.768$	-	4.0	9	Palanche, Berman and Frondel (1944)
Gamma Alumina	Al_2O_3	Cubic	$n_D=1.696$		3.4		Fricke and Hüttig (1944)
Diaspore (Beta-alumina monohydrate)	$Al_2O_3 \cdot H_2O$	Orthorhombic	$\alpha=1.702$[b] $\beta=1.722$ $\gamma=1.750$	+	3.4	6.5 - 7	Palanche, Berman, and Frondel (1944)
Boehmite (Alpha-alumina monohydrate)	$Al_2O_3 \cdot H_2O$	Orthorhombic	$\alpha=1.646$ $\gamma=1.661$	-	3.02	3.5 - 4	Bohnstedt, Kupletskaya and Vlodavetz (1945)
			$\alpha=1.649$ $\beta=1.659$[c] $\gamma=1.665$				Ervin and Osborne (1951)
Gibbsite (alpha-alumina trihydrate)	$Al_2O_3 \cdot 3H_2O$	Monoclinic	$\alpha=1.568$ $\beta=1.568$ $\gamma=1.587$	+	2.4	3	Palanche, Berman, and Frondel (1944)
Bayerite (Beta-alumina trihydrate)	$Al_2O_3 \cdot 3H_2O$	Hexagonal	$n=1.583$	-	2.5		Montero (1942)

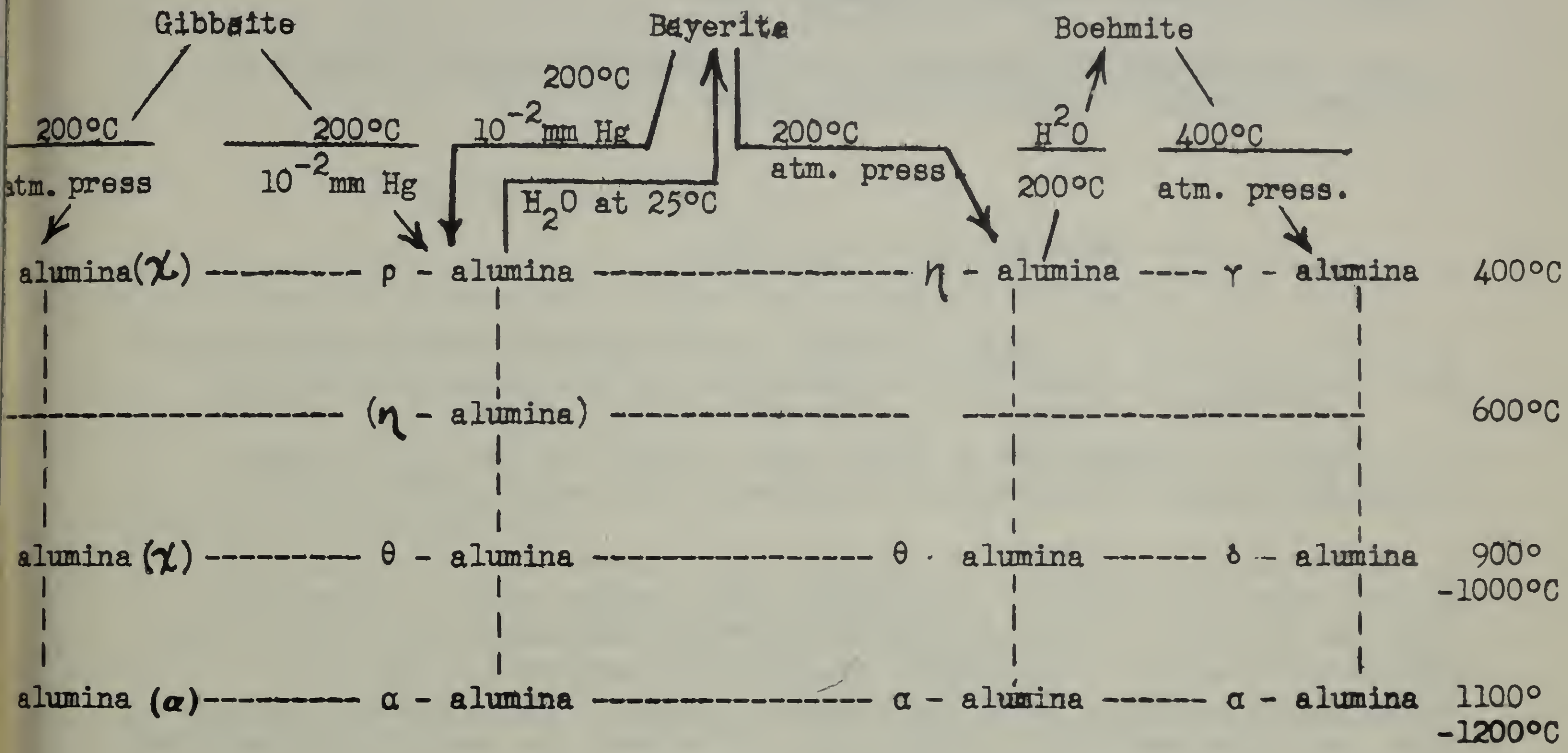
a.) ε is the extraordinary light path, and ω the ordinary light path through a uniaxial crystal system.

b.) α, β, and γ are the optical axes of a biaxial crystal system.

c.) Misprint in Ref. [2]; corrected by Ref. [1].

Table 3

Transformations upon dehydration and rehydration of alumina and its hydrates



1.) Gibbsite, alpha-$Al_2O_3 \cdot 3H_2O$

a) Prepare aluminum hydroxide gel by reacting aluminum nitrate with ammonium hydroxide. The gel is heated for 6 days at 110°C at a water pressure of 20.8 psi to yield gibbsite [2].

b) In the majority of references this compound was either prepared by the Bayer process or obtained commercially.

2.) Bayerite, beta-$Al_2O_3 \cdot 3H_2O$

a) Carbon dioxide is bubbled through a cold solution of sodium aluminate. The precipitate is washed free of carbonate ion and dried at 110°C [11].

b) Gibbsite is dehydrated at 200°C under vacuum (10^{-2} mm Hg) to yield rho-alumina which is rehydrated to bayerite with water at 25°C [3].

c) Aluminum foil (99.99%) is cut into small pieces and degreased with freshly distilled acetone. Amalgamate the aluminum with 0.1 N mercuric chloride solution. Wash thoroughly with distilled water and finally with conductivity water. The washed, amalgamated aluminum is placed in conductivity water protected from carbon dioxide. The product separates as a gray substance which becomes pure white when the reaction is completed. This takes about a day. The amorphous gel passes over to bayerite on standing [12].

3.) Boehmite, alpha-$Al_2O_3 \cdot H_2O$

a) Gibbsite is heated for 8 days at 140°C with water at a pressure of 52 psi, or gamma-alumina (see 6) or hydrated alumina gel (see 1.a.) is heated for 120 hours at 285°C and under a water vapor pressure of 1500 psi [2].

b) Gibbsite is rapidly ignited under vacuum at 200°C. The heating is continued for 16 hours [13].

c) By digestion of the alpha-alumina trihydrate in water at 200°C [5].

4.) Diaspore, beta-$Al_2O_3 \cdot H_2O$

a) Diaspore crystallizes from the systems NaOH-H_2O-Al_2O_3 and Na_2CO_3-H_2O-Al_2O_3 when sealed in a silver tube enclosed in a thermostated autoclave. Before sealing the tube, a seed of corundum crystal with the desired orientation is mounted in the inner tube. The concentration of the sodium hydroxide or sodium carbonate solution should be between 1 and 2 molar. The inner tube should be between 0.70 and 0.85 percent full [14].

5.) Corundum, alpha-Al_2O_3

a) Gamma-alumina (see 6) or aluminum hydroxide gel (see 1.a.) are heated for 47 hours at 440°C under a water vapor pressure of 450 psi [2]. Fine grain diaspore crystals were used as seeds.

b) Gibbsite is heated for one hour in dry air or steam at 1200°C [5].

c) Any of the forms of alumina when heated in air at 1100° to 1200°C are converted to corundum [3].

6.) Gamma-alumina, gamma-Al_2O_3

a) By slow dehydration of boehmite at atmospheric pressure at temperatures up to 400°C [3].

b) Boehmite is prepared by the ignition of gibbsite under vacuum. On subsequent ignition to 550°C in air, the boehmite decomposes to gamma-alumina [13].

c) The gelatinous boehmite precipitate is heated in dry air at 600°C for an hour [5].

7.) Eta-alumina, eta-Al_2O_3

Eta-alumina is prepared by slow dehydration of bayerite at 200°C under atmospheric pressure [3].

8.) Delta-alumina, delta-Al_2O_3

a) Delta-alumina may be prepared by progressively heating gamma-alumina in air from 400° to 900°C [3].

b) By heating a gelatinous precipitate of boehmite at 1200° for one hour [5].

9.) Chi-alumina, chi-Al_2O_3

Chi-alumina is prepared by slow dehydration of gibbsite under atmospheric pressure and temperatures up to 900°C [3].

10.) Theta-alumina, theta-Al_2O_3

a) Precipitated bayerite heated in steam for one hour at 1000°C yields theta-alumina [5].

b) By heating eta-alumina up to 900°C in air [4].

Alumina and Its Hydrates

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B. Beryllium Oxide and Hydroxide.

Literature on the preparation of the oxide and hydroxide of beryllium is limited. It seems that they can be obtained commercially in fairly pure states, thus reducing the handling of these beryllium compounds which are considered toxic.

Apparently there is only one form of beryllium oxide, but there are literature references to α- and β- beryllium hydroxide. Beryllium oxide forms hexagonal crystals when heated near its melting point (2530°C). The density of the oxide is around 3.18 g/cc.

Some procedures for preparing beryllium oxide and beryllium hydroxide are given in the following section

1. Beryllium Oxide

a) Dehydrate beryllium hydroxide (See 2a) by heating slowly up to 800°C to obtain the oxide, 95-97 percent pure(1).

b) Dehydrate beryllium hydroxide (See 2b) to oxide.

c) Beryllium oxide of exceptional fineness and high purity are produced by introducing $BeCl_2$ vapor under its own vapor pressure or carried in a stream of preheated air into an empty tubular insulated reactor, surrounded by an annular blanket of flame produced by burning a gaseous mixture of hydrocarbon and oxygen. There must be sufficient hydrocarbon to insure complete hydrolysis of all the hydrolyzable halides and sufficient oxygen for complete combustion of all the hydrocarbon(3).

2. Beryllium Hydroxide

a) Electrolyze in a cell with graphite electrodes, with an aqueous solution of sodium chloride in the anode compartment and a solution of sodium fluoberyllate (Na_2BeF_4) in the cathode compartment. The current density may be varied from 1 to 12 amp. per sq. decimeter. Filter, wash thoroughly and dry the beryllium hydroxide precipitate from the cathode compartment(1).

b) Electrolyze a solution of beryllium salt in a S-shaped cell under the following conditions: 20 to 2000 v, 25 to 30 ma, and for 3-30 days. The beryllium hydroxide is obtained in a crystalline state at the cathode(2).

Beryllium Oxide and Hydroxide

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C. Magnesium Oxide and Hydroxide

Very little appears in the recent literature regarding the preparation and purification of MgO and $Mg(OH)_2$. However, it would seem that the same general techniques as are employed in the preparation and purification of the lithium oxide and hydroxide could be employed. If magnesium of sufficient purity cannot be obtained industrially, it could probably be purified by zone-melting techniques. As with all alkali or alkaline earth hydroxides, carbon dioxide must be kept out of contact with them. With the oxides, water also must be absent.

Magnesium hydroxide occurs in a hydrated form, although the degree of hydration is not uniform. A method of preparing crystalline magnesium hydroxide is presented in a British Patent[1], although the language of the abstract is vague.

Magnesium oxide is prepared by thermal decomposition of the hydroxide, carbonate or nitrate. This method of preparation yields a fluffy microcrystalline powder. Magnesium oxide may be prepared in a crystalline form of density 3.56 g/cc[2] by heating nearly to the melting point (2800°C).

Magnesium Oxide and Hydroxide

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D. Lithium Oxide and Lithium Hydroxide

There are five well known compounds of lithium, hydrogen, and oxygen: lithium hydroperoxide monohydrate (LiO_2H-H_2O), lithium peroxide (Li_2O_2), lithium hydroxide monohydrate ($LiOH\cdot H_2O$), anhydrous lithium hydroxide ($LiOH$), and lithium oxide (Li_2O).

These compounds may all be prepared either from pure lithium metal or lithium hydroxide which is available commercially (Metalloy Corporation). Upon heating, the more highly hydrated or oxidized form exists in equilibrium with the vapor, hence, in order to push the reaction to completion these vapors must be removed. At the same time, extreme care must be used to protect the products from water vapor or carbon dioxide.

1) Preparation of lithium hydroperoxide monohydrate: This material is prepared by dissolving pure lithium metal in alcohol until the precipitate of lithium ethylate becomes very heavy. In some cases it is desirable to filter and dry the lithium ethylate. In either case, 30% hydrogen peroxide is added to an alcoholic suspension of lithium ethylate and the resulting lithium hydroperoxide monohydrate is filtered. All reactions are carried out in a CO_2 free helium atmosphere, Lithium hydroperoxide monohydrate is stable in contact with the mother liquor, but decomposes upon drying[1].

2) Preparation of lithium peroxide: This material was prepared by dehydrating lithium hydroperoxide monohydrate in a dessicator over P_2O_5 at 20 mm pressure. The reaction is quantitative and the product may be preserved indefinitely in the dark under refrigeration. Lithium peroxide has a density of 2.26 g/cc at 25°[1]. At 225°-235°C a transition from α to β-Li_2O_2 occurs, and at 315° to 342°C a strongly endothermic decomposition occurs. This decomposition is complete at 450°C[2].

3) Preparation of lithium hydroxide monohydrate: This material was prepared by dissolving pure lithium metal in distilled water until the precipitate became heavy, and further solution of the metal takes place slowly. The precipitate is dried over P_2O_5 in a dessicator at 20 mm Hg until only a moist solid remains. The remaining excess water is removed by drying in a vacuum dessicator over anhydrous lithium hydroxide until equilibrium is reached[1].

Lithium hydroxide monohydrate was also prepared by multiple crystallization of commercial pure lithium hydroxide (Metalloy Corporation) in distilled water[3].

4) Preparation of anhydrous lithium hydroxide: This material is prepared by the dehydration of the monohydrate under a stream of CO_2-free helium gas, Cohen[1] heated the monohydrate in a platinum crucible at 140°C. The evolved water was collected and weighed to follow the degree of dehydration. Shomate and Cohen[4] heated the monohydrate to 350°C over a 24 hour period. All of these dehydrations were carried out in a CO_2-free helium atmosphere.

5) Preparation of lithium oxide:

a) From lithium hydroxide: Lithium hydroxide monohydrate was heated in a nickel boat under an atmosphere of hydrogen gas, first at about 150°C and finally at 800°C[3].

b) From lithium peroxide: Lithium peroxide was placed in a gold capsule and the temperature raised to 550°C over a period of 4 hours. The water vapor was carried away by a stream of helium[4]. Another procedure was to heat slowly the peroxide in an alundum combustion boat to 450°C and hold it at that temperature for six hours. With lithium oxide more than any of the others, scrupulous care must be taken to eliminate carbon dioxide and water.

Lithium Oxide and Hydroxide

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II. Chlorides, Fluorides and Hydrides of Aluminum, Beryllium, Magnesium and Lithium

A. Chlorides

The chlorides of the light metals can generally be obtained commercially in high purity. However, requirements of 99.5% or better purity may necessitate further purification. The main problem in preparing and keeping pure anhydrous chlorides of these metals is their tendency towards hydrolysis which results in the formation of basic chlorides. To eliminate this contamination several methods may be employed. The simplest is careful, repeated vacuum sublimation. However, this method may not eliminate some oxychlorides which may be sufficiently volatile. Another approach is the heating of relatively pure chlorides in a stream of dry $HC\ell$ gas or with $NH_4C\ell$. Finally if neither of the above methods leads to satisfactory products the materials can be synthesized directly from the highly purified metals by direct reaction with chlorine or $HC\ell$ gas.

B. Fluorides

Like the chlorides the fluorides are also available commercially. Their preparation for the most part can be accomplished by direct reaction of the metal with fluorine or HF, or by the treatment of oxides or carbonates with aqueous HF. In the latter case hydrates may form and elimination of water can also lead to the formation of basic fluorides. Here again heating in an atmosphere of anhydrous HF will lead to pure fluorides. The general procedures for purification listed for the chlorides are applicable here too.

C. Hydrides

The synthesis of pure hydrides poses a considerably greater problem caused mainly by their thermal instability and high reactivity. Synthesis by direct union of the elements has been accomplished for Li and Mg, but not for Be and Al so far. For the latter two, indirect methods have been employed which generally lead to contaminated products.

1) $A\ell H_3$

Although there is a reference in the patent literature to the preparation of aluminum hydride by the treatment of aluminum with hydrogen[1], it is very unlikely that a satisfactory product can be obtained by this method. The most common procedure involves the reduction of aluminum chloride with lithium aluminum hydride in ether[2].

$3LiA\ell H_4 + A\ell C\ell_3 \xrightarrow{Et2O} 4A\ell H_3 + 3LiC\ell$. Polymeric $(A\ell H_3)_x$ precipitates out of the ether solution in the above synthesis. Prolonged drying and heating failed to remove all the ether without causing appreciable decomposition. It is believed that the ether is present in the form of an etherate which lends the $A\ell H_3$ additional stability. Attempts to prepare ether free products failed for the most part. In one case a different route to synthesis was employed utilizing the formation of a volatile hydride[3].

$4LiA\ell H_4 + SiC\ell_4 \longrightarrow SiH_4 + 4A\ell H_3 + 4LiC\ell$. This method appears to have led to a nearly ether-free product which, however, was less stable. The decomposition of $A\ell H_3$ is reported to occur above 100°C but this refers to materials containing fair amounts of ether.

As it appears doubtful that pure $A\ell H_3$ can be prepared, it may be necessary to use compounds of $A\ell H_3$ which can be prepared in higher purity. Such compounds may be found among the complexes which are formed by $A\ell H_3$, notably those with trimethylamine, ~~tetrahydrofuran, and aluminum~~ chloride[4].

The structure of polymeric $(A\ell H_3)_x$ is still in doubt. The most frequent suggestion is that of a hydrogen bridge network which is highly cross linked.

2) BeH_2

The first preparations of BeH_2 involved the reduction of $BeC\ell_2$ or $BeMe_2$ with LiH, $LiA\ell H_4$ or $Me_2A\ell H$[5,6]. All these reactions have to be performed in ether solution and the resulting product could not be satisfactorily freed from ether. A better method involves the pyrolysis of dialkyl beryllium compounds, especially that of di, t-butylberyllium[7,8].

$$\left[(CH_3)_3C\right]_2 Be \xrightarrow{210°C} BeH_2 + 2(CH_3)_2C = CH_2$$

This method can be applied to the etherate or the ether-free material with satisfactory results. The purity obtained is about 80% by weight or 97-99 mole%. Furthermore, this method yields a more stable product which does not decompose up to 240°C.

Beryllium hydride, like aluminum hydride, is believed to have a hydrogen bridge structure[9]. The compound can thus be best visualized as a polymer rather than a salt.

3) MgH_2

This hydride can be synthesized either by the pyrolysis of diethyl magnesium or the Grignard reagent[10]

$$(C_2H_5)_2\,Mg \xrightarrow{220^\circ C} MgH_2 + 2C_2H_4$$

$$2C_2H_5MgX \xrightarrow{220^\circ C} MgH_2 + 2C_2H_4 + MgX_2$$

or by direct union of the elements with or without MgI_2 as catalyst[11,12]

$$Mg + H_2 \xrightarrow[450^\circ C]{68\ atm} MgH_2$$

However, the purity of the product is not indicated. It is feasible that it contains some free magnesium. Decomposition of MgH_2 starts at about 280°C.

4) LiH

This compound can be prepared in 99.6 ±0.2% purity, (based on H_2 analysis) by direct union of the elements at about 700°C. LiH melts at 688 ±1°C [13,14].

5) $LiA\ell H_4$

Lithium aluminum hydride can be synthesized by the reduction of aluminum chloride or bromide with lithium hydride in ether[2,15].

$$4LiH + A\ell C\ell_3 \xrightarrow{Et_2O} LiA\ell H_4 + 3LiC\ell$$

The ether solution of the product can be evaporated to dryness to obtain the solid. Purity of about 99% has been attained by a repeated process of filtration, evaporation, and solution[16]. The material is stable to around 100°C. A commercial product of about 95% purity can be obtained which could be purified by several recrystallizations.

Chlorides, Fluorides, and Hydrides of Aluminum, Beryllium, Magnesium, and Lithium

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CHAPTER VIII

IDEAL GAS THERMODYNAMIC FUNCTIONS

Joseph Hilsenrath and William H. Evans

The thermodynamic functions for the diatomic molecules AlF, BeF, MgF, AlCl, BeCl, MgCl, AlO, BeO, and MgO, which are contained in this section have been newly computed from the molecular constants listed and discussed in Chapter IV. Since these molecular constants are for the ground state and have been adjusted for the naturally occurring isotopic abundances, the tables are correspondingly for the ground state and for the normal isotopic mixture. However, as usual, the effects of nuclear spin and isotopic mixing have not been included.

The thermodynamic functions, $-(F^{\circ}-H_0^{\circ})/RT$, $(H^{\circ}-H_0^{\circ})/RT$, S°/R, $(H^{\circ}-H_0^{\circ})/R$, and C_p°/R, have been computed from formulas based on the Mayer and Mayer treatment for diatomic molecules. The tables included first order corrections to the harmonic oscilator-rigid rotator for: vibrational anharmonicity, rotational stretching, and rotation-vibration interaction computed in the following manner:

Translational and rotational contributions:-

$$-(F^{\circ}-H_0^{\circ})/RT = 1.5\ell nM + 2.5\ell nT - 3.6644173 - \ell n\sigma + \sigma/3 + \sigma^2/90$$

$$(H^{\circ}-H_0^{\circ})/RT = 3.5 - \sigma/3 - \sigma^2/45$$

$$C_p^{\circ}/R = 3.5 + \sigma^2/45$$

where $\sigma = (B_e - \alpha_e/2)hc/kT$, and $hc/k = 1.43880$ cm deg.K.

Vibrational contributions:-

$$-(F^{\circ}-H_0^{\circ})/RT = \ell n(1 - e^{-u})$$

$$(H^{\circ}-H_0^{\circ})/RT = ue^{-u}/(1 - e^{-u})$$

$$C_p^{\circ}/R = u^2e^{-u}/(1 - e^{-u})^2$$

where $u = (\omega_e - 2x_e\omega_e)hc/kT$.

Anharmonicity corrections:

$$-(F^{\circ}-H_0^{\circ})/RT = 8\gamma^2/\sigma + \delta e^{-u}/(1 - e^{-u}) + 2Xue^{-2u}/(1 - e^{-u})^2$$

$$(H^{\circ}-H^{\circ}_{0})/RT = 8\gamma^{2}/\sigma + \delta u e^{-u}/(1 - e^{-u})^{2} + 4Xu^{2}e^{-2u}/(1 - e^{-u})^{3}$$

$$- 2Xue^{-2u}/(1 - e^{-u})^{2}$$

$$C^{\circ}_{p}/R = 16\gamma^{2}/\sigma - \delta u^{2}e^{-u}/(1 - e^{-u})^{2} + 2\delta u^{2}e^{-u}/(1 - e^{-u})^{3}$$

$$- 8Xu^{2}e^{-2u}/(1 - e^{-u})^{3} - 4Xu^{3}e^{-2u}/(1 - e^{-u})^{3}$$

$$+ 12Xu^{3}e^{-2u}/(1 - e^{-u})^{4}$$

where

$$\delta = \alpha_{e}/B_{e}$$

$$8\gamma^{2} = 2D_{e}/B_{e}$$

$$X = \omega_{e}x_{e}/\omega_{e}.$$

The tabulated values of the entropy were computed from the relation

$$S^{\circ}/R = (H^{\circ}-H^{\circ}_{0})/RT - (F^{\circ}-H^{\circ}_{0})/RT.$$

The thermodynamic tables presented here represent only a part of the tables which are projected for the near future. These will include ideal gas thermal functions for the remaining molecules surveyed in Chapter IV, thermodynamic properties of the liquid and solid phases for these molecules, and their vapor pressures.

Until such time as these new NBS tables become available, the reader is referred to Appendix I which provides an indexed bibliography, largely of compendia, of thermal functions for important inorganic and organic molecules. While the list is not critical, it is selective and does include most, if not all, of the recent collections of tables of thermodynamic functions.

Table 1. Thermodynamic Functions for Li_2

T °K	$\frac{-(F^o-H_0^o)}{RT}$	$\frac{H^o-H_0^o}{RT}$	$\frac{S^o}{R}$	$\frac{H^o-H_0^o}{R}$	$\frac{C_p^o}{R}$
50.	13.314	3.494	16.808	174.7	3.505
75.	14.732	3.504	18.236	262.8	3.557
100.	15.743	3.531	19.274	353.1	3.672
125.	16.536	3.573	20.108	446.6	3.808
150.	17.191	3.623	20.814	543.4	3.933
175.	17.754	3.675	21.428	643.1	4.038
200.	18.248	3.726	21.973	745.1	4.122
225.	18.689	3.773	22.463	849.0	4.190
250.	19.089	3.818	22.907	954.5	4.244
275.	19.455	3.859	23.314	1061.1	4.288
300.	19.792	3.896	23.688	1168.8	4.324
325.	20.106	3.930	24.036	1277.3	4.353
350.	20.398	3.961	24.359	1386.4	4.378
375.	20.672	3.990	24.662	1496.2	4.399
400.	20.931	4.016	24.947	1606.4	4.417
425.	21.175	4.040	25.215	1717.0	4.433
450.	21.406	4.062	25.469	1828.0	4.447
475.	21.627	4.083	25.709	1939.3	4.459
500.	21.837	4.102	25.938	2051.0	4.470
550.	22.229	4.136	26.365	2274.9	4.489
600.	22.590	4.166	26.757	2499.8	4.504
650.	22.925	4.193	27.118	2725.3	4.518
700.	23.237	4.216	27.453	2951.5	4.529
750.	23.528	4.238	27.766	3178.3	4.540
800.	23.802	4.257	28.059	3405.5	4.550
850.	24.061	4.274	28.335	3633.2	4.558
900.	24.306	4.290	28.596	3861.3	4.567
950.	24.538	4.305	28.843	4089.9	4.574
1000.	24.759	4.319	29.078	4318.8	4.582
1050.	24.970	4.331	29.302	4548.0	4.589
1100.	25.172	4.343	29.515	4777.7	4.596
1150.	25.365	4.354	29.720	5007.6	4.602
1200.	25.551	4.365	29.916	5237.9	4.609
1250.	25.729	4.375	30.104	5468.5	4.615
1300.	25.901	4.384	30.285	5699.4	4.621
1350.	26.067	4.393	30.460	5930.6	4.627
1400.	26.227	4.402	30.628	6162.2	4.633
1450.	26.381	4.410	30.791	6394.0	4.639
1500.	26.531	4.417	30.948	6626.1	4.645
1550.	26.676	4.425	31.101	6858.5	4.651
1600.	26.816	4.432	31.248	7091.2	4.657
1650.	26.953	4.439	31.392	7324.1	4.662
1700.	27.085	4.446	31.531	7557.4	4.668
1750.	27.214	4.452	31.666	7790.9	4.673
1800.	27.340	4.458	31.798	8024.7	4.679
1850.	27.462	4.464	31.926	8258.8	4.684
1900.	27.581	4.470	32.051	8493.2	4.690
1950.	27.697	4.476	32.173	8727.8	4.695
2000.	27.811	4.481	32.292	8962.7	4.701
2050.	27.922	4.487	32.408	9197.9	4.706
2100.	28.030	4.492	32.522	9433.3	4.712
2150.	28.136	4.497	32.633	9669.0	4.717
2200.	28.239	4.502	32.741	9905.0	4.722
2250.	28.340	4.507	32.847	10141.2	4.728
2300.	28.439	4.512	32.951	10377.8	4.733
2350.	28.536	4.517	33.053	10614.5	4.738

This table has been computed for the ground state of the molecule, which is taken as $^1\Sigma$, using the following molecular constants: $B_e = 0.6796 \text{ cm}^{-1}$, $\alpha_e = 0.00731 \text{ cm}^{-1}$, $D_e = 10.07 \times 10^{-6} \text{ cm}^{-1}$, $\omega_e x_e = 2.627 \text{ cm}^{-1}$, and $\omega_e = 353.121 \text{ cm}^{-1}$. See reverse side for conversion factors.

Table 1. Thermodynamic Functions for Li_2 - Continued

T °K	$\frac{-(F^{\circ}-H^{\circ}_{0})}{RT}$	$\frac{H^{\circ}-H^{\circ}_{0}}{RT}$	$\frac{S^{\circ}}{R}$	$\frac{H^{\circ}-H^{\circ}_{0}}{R}$	$\frac{C^{\circ}_{p}}{R}$
2400.	28.632	4.521	33.153	10851.6	4.744
2450.	28.725	4.526	33.251	11088.9	4.749
2500.	28.816	4.531	33.347	11326.5	4.754
2600.	28.994	4.539	33.534	11802.4	4.765
2700.	29.166	4.548	33.714	12279.4	4.775
2800.	29.331	4.556	33.887	12757.5	4.786
2900.	29.491	4.564	34.056	13236.6	4.796
3000.	29.646	4.572	34.218	13716.7	4.807
3100.	29.796	4.580	34.376	14197.9	4.817
3200.	29.942	4.588	34.529	14680.2	4.828
3300.	30.083	4.595	34.678	15163.4	4.838
3400.	30.220	4.602	34.823	15647.8	4.848
3500.	30.354	4.609	34.963	16133.1	4.859
3600.	30.484	4.617	35.100	16619.5	4.869
3700.	30.610	4.624	35.234	17107.0	4.880
3800.	30.734	4.630	35.364	17595.5	4.890
3900.	30.854	4.637	35.491	18085.0	4.900
4000.	30.972	4.644	35.615	18575.6	4.911
4100.	31.086	4.651	35.737	19067.2	4.921
4200.	31.198	4.657	35.856	19559.8	4.932
4300.	31.308	4.664	35.972	20053.5	4.942
4400.	31.415	4.670	36.085	20548.2	4.952
4500.	31.520	4.676	36.197	21043.9	4.963
4600.	31.623	4.683	36.306	21540.7	4.973
4700.	31.724	4.689	36.413	22038.5	4.983
4800.	31.823	4.695	36.518	22537.4	4.994
4900.	31.920	4.701	36.621	23037.3	5.004
5000.	32.015	4.708	36.722	23538.2	5.014
5100.	32.108	4.714	36.822	24040.1	5.025
5200.	32.200	4.720	36.919	24543.1	5.035
5300.	32.290	4.726	37.015	25047.1	5.045
5400.	32.378	4.732	37.110	25552.2	5.056
5500.	32.465	4.738	37.203	26058.3	5.066
5600.	32.550	4.744	37.294	26565.4	5.076
5700.	32.634	4.750	37.384	27073.6	5.087
5800.	32.717	4.756	37.473	27582.7	5.097
5900.	32.798	4.762	37.560	28093.0	5.107
6000.	32.878	4.767	37.646	28604.2	5.118
273.15	19.429	3.856	23.285	1053.2	4.285
298.15	19.768	3.893	23.662	1160.8	4.321

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal $mole^{-1}$ $°K^{-1}$ (or $°C^{-1}$)	1.98726
cal g^{-1} $°K^{-1}$ (or $°C^{-1}$)	0.14317
joules g^{-1} $°K^{-1}$ (or $°C^{-1}$)	0.59902
Btu $(lb\ mole)^{-1}$ $°R^{-1}$ (or $°F^{-1}$)	1.98595
Btu lb^{-1} $°R^{-1}$ (or $°F^{-1}$)	0.14308

Table 2. Thermodynamic Functions for LiF

T °K	$\frac{-(F^\circ - H_0^\circ)}{RT}$	$\frac{H^\circ - H_0^\circ}{RT}$	$\frac{S^\circ}{R}$	$\frac{H^\circ - H_0^\circ}{R}$	$\frac{C_p^\circ}{R}$
50.	14.214	3.487	17.701	174.3	3.501
75.	15.629	3.492	19.121	261.9	3.502
100.	16.634	3.494	20.128	349.4	3.502
125.	17.414	3.496	20.910	437.0	3.506
150.	18.051	3.499	21.550	524.8	3.518
175.	18.591	3.503	22.094	613.0	3.540
200.	19.059	3.510	22.569	701.9	3.574
225.	19.473	3.519	22.992	791.8	3.618
250.	19.844	3.531	23.376	882.9	3.667
275.	20.182	3.546	23.728	975.2	3.721
300.	20.491	3.563	24.054	1068.9	3.775
325.	20.777	3.581	24.358	1163.9	3.828
350.	21.043	3.601	24.644	1260.3	3.879
375.	21.292	3.621	24.913	1357.9	3.927
400.	21.526	3.642	25.168	1456.6	3.972
425.	21.748	3.662	25.410	1556.5	4.014
450.	21.958	3.683	25.641	1657.3	4.053
475.	22.157	3.703	25.861	1759.1	4.088
500.	22.348	3.723	26.071	1861.7	4.121
550.	22.705	3.762	26.467	2069.2	4.178
600.	23.033	3.799	26.832	2279.3	4.226
650.	23.339	3.833	27.172	2491.6	4.267
700.	23.624	3.866	27.490	2705.9	4.301
750.	23.892	3.896	27.787	2921.7	4.331
800.	24.144	3.924	28.068	3138.9	4.357
850.	24.383	3.950	28.333	3357.3	4.379
900.	24.609	3.974	28.584	3576.8	4.399
950.	24.825	3.997	28.822	3797.2	4.417
1000.	25.030	4.018	29.049	4018.4	4.432
1050.	25.227	4.039	29.265	4240.4	4.446
1100.	25.415	4.057	29.473	4463.1	4.459
1150.	25.596	4.075	29.671	4686.3	4.471
1200.	25.770	4.092	29.862	4910.1	4.481
1250.	25.937	4.108	30.045	5134.5	4.491
1300.	26.099	4.122	30.221	5359.2	4.500
1350.	26.254	4.137	30.391	5584.5	4.509
1400.	26.405	4.150	30.555	5810.1	4.517
1450.	26.551	4.163	30.714	6036.1	4.524
1500.	26.692	4.175	30.867	6262.5	4.531
1550.	26.829	4.187	31.016	6489.3	4.538
1600.	26.962	4.198	31.160	6716.3	4.544
1650.	27.092	4.208	31.300	6943.7	4.550
1700.	27.218	4.218	31.436	7171.3	4.556
1750.	27.340	4.228	31.568	7399.3	4.562
1800.	27.459	4.238	31.697	7627.5	4.567
1850.	27.575	4.246	31.822	7856.0	4.572
1900.	27.689	4.255	31.944	8084.7	4.577
1950.	27.799	4.263	32.063	8313.7	4.582
2000.	27.908	4.271	32.179	8543.0	4.587
2050.	28.013	4.279	32.292	8772.4	4.592
2100.	28.116	4.287	32.403	9002.1	4.596
2150.	28.217	4.294	32.511	9232.1	4.601
2200.	28.316	4.301	32.617	9462.2	4.605
2250.	28.413	4.308	32.721	9692.5	4.609
2300.	28.508	4.314	32.822	9923.1	4.613
2350.	28.600	4.321	32.921	10153.9	4.617
2400.	28.691	4.327	33.018	10384.9	4.622

This table has been computed for the ground state of the molecule, which is taken as $^1\Sigma$, using the following molecular constants: B_e = 1.4221 cm^{-1}, α_e = 0.015 cm^{-1}, D_e = 14.20 x 10^{-6} cm^{-1}, $\omega_e x_e$ = 7.0 cm^{-1}, and ω_e = 900.0 cm^{-1}. See reverse side for conversion factors.

Table 2. Thermodynamic Functions for LiF - Continued

T °K	$\frac{-(F^o-H^o_0)}{RT}$	$\frac{H^o-H^o_0}{RT}$	$\frac{S^o}{R}$	$\frac{H^o-H^o_0}{R}$	$\frac{C^o_p}{R}$
2450.	28.781	4.333	33.114	10616.0	4.626
2500.	28.868	4.339	33.207	10847.4	4.629
2600.	29.039	4.350	33.389	11310.7	4.637
2700.	29.203	4.361	33.564	11774.8	4.645
2800.	29.362	4.371	33.733	12239.7	4.652
2900.	29.515	4.381	33.897	12705.2	4.659
3000.	29.664	4.391	34.055	13171.5	4.666
3100.	29.808	4.400	34.208	13638.5	4.673
3200.	29.948	4.408	34.356	14106.2	4.680
3300.	30.084	4.417	34.500	14574.6	4.687
3400.	30.216	4.425	34.640	15043.6	4.694
3500.	30.344	4.432	34.777	15513.4	4.701
3600.	30.469	4.440	34.909	15983.8	4.707
3700.	30.591	4.447	35.038	16454.8	4.714
3800.	30.710	4.454	35.164	16926.6	4.721
3900.	30.825	4.461	35.287	17399.0	4.727
4000.	30.938	4.468	35.406	17872.0	4.734
4100.	31.049	4.475	35.523	18345.7	4.740
4200.	31.157	4.481	35.638	18820.0	4.747
4300.	31.262	4.487	35.749	19295.0	4.753
4400.	31.365	4.493	35.859	19770.6	4.759
4500.	31.467	4.499	35.966	20246.9	4.766
4600.	31.565	4.505	36.071	20723.8	4.772
4700.	31.662	4.511	36.173	21201.3	4.778
4800.	31.757	4.517	36.274	21679.5	4.785
4900.	31.851	4.522	36.373	22158.2	4.791
5000.	31.942	4.528	36.470	22637.7	4.797
5100.	32.032	4.533	36.565	23117.7	4.804
5200.	32.120	4.538	36.658	23598.4	4.810
5300.	32.206	4.543	36.750	24079.7	4.816
5400.	32.291	4.548	36.840	24561.6	4.822
5500.	32.375	4.553	36.928	25044.1	4.829
5600.	32.457	4.558	37.015	25527.3	4.835
5700.	32.538	4.563	37.101	26011.1	4.841
5800.	32.617	4.568	37.185	26495.5	4.847
5900.	32.695	4.573	37.268	26980.6	4.853
6000.	32.772	4.578	37.350	27466.2	4.860
273.15	20.158	3.545	23.703	968.3	3.717
298.15	20.469	3.562	24.031	1061.9	3.771

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal mole^{-1} $°K^{-1}$ (or $°C^{-1}$)	1.98726
cal g^{-1} $°K^{-1}$ (or $°C^{-1}$)	0.076610
joules g^{-1} $°K^{-1}$ (or $°C^{-1}$)	0.320536
Btu $(\text{lb mole})^{-1}$ $°R^{-1}$ (or $°F^{-1}$)	1.98595
Btu lb^{-1} $°R^{-1}$ (or $°F^{-1}$)	0.076559

Table 3. Thermodynamic Functions for LiCl

T °K	$\frac{-(F^o-E_0^o)}{RT}$	$\frac{H^o-E_0^o}{RT}$	$\frac{S^o}{R}$	$\frac{H^o-E_0^o}{R}$	$\frac{C_p^o}{R}$
50.	15.637	3.494	19.131	174.7	3.501
75.	17.055	3.496	20.551	262.2	3.502
100.	18.061	3.498	21.559	349.8	3.510
125.	18.842	3.503	22.345	437.9	3.537
150.	19.481	3.512	22.994	526.9	3.584
175.	20.024	3.527	23.551	617.2	3.649
200.	20.496	3.547	24.043	709.4	3.721
225.	20.915	3.570	24.485	803.3	3.795
250.	21.292	3.596	24.889	899.1	3.867
275.	21.637	3.624	25.261	996.6	3.933
300.	21.953	3.652	25.605	1095.7	3.993
325.	22.247	3.681	25.927	1196.2	4.047
350.	22.520	3.709	26.229	1298.0	4.094
375.	22.777	3.736	26.513	1400.9	4.137
400.	23.019	3.762	26.781	1504.8	4.174
425.	23.248	3.787	27.035	1609.6	4.208
450.	23.465	3.811	27.277	1715.1	4.237
475.	23.672	3.835	27.506	1821.4	4.264
500.	23.869	3.857	27.726	1928.3	4.287
550.	24.239	3.898	28.136	2143.7	4.328
600.	24.579	3.935	28.514	2361.0	4.361
650.	24.896	3.969	28.864	2579.7	4.388
700.	25.191	4.000	29.190	2799.7	4.411
750.	25.468	4.028	29.495	3020.7	4.430
800.	25.729	4.053	29.782	3242.6	4.447
850.	25.975	4.077	30.052	3465.4	4.462
900.	26.209	4.099	30.307	3688.8	4.475
950.	26.431	4.119	30.550	3912.8	4.486
1000.	26.643	4.137	30.780	4137.4	4.497
1050.	26.845	4.155	31.000	4362.5	4.506
1100.	27.038	4.171	31.209	4588.0	4.515
1150.	27.224	4.186	31.410	4814.0	4.523
1200.	27.403	4.200	31.603	5040.3	4.531
1250.	27.574	4.214	31.788	5267.0	4.538
1300.	27.740	4.226	31.966	5494.1	4.544
1350.	27.900	4.238	32.138	5721.4	4.551
1400.	28.054	4.249	32.303	5949.1	4.557
1450.	28.203	4.260	32.463	6177.1	4.562
1500.	28.348	4.270	32.618	6405.4	4.568
1550.	28.488	4.280	32.768	6633.9	4.573
1600.	28.624	4.289	32.913	6862.7	4.578
1650.	28.756	4.298	33.054	7091.7	4.583
1700.	28.885	4.306	33.191	7321.0	4.588
1750.	29.010	4.315	33.324	7550.5	4.593
1800.	29.131	4.322	33.454	7780.3	4.597
1850.	29.250	4.330	33.580	8010.2	4.602
1900.	29.365	4.337	33.702	8240.4	4.606
1950.	29.478	4.344	33.822	8470.8	4.611
2000.	29.588	4.351	33.939	8701.5	4.615
2050.	29.696	4.357	34.053	8932.3	4.619
2100.	29.801	4.364	34.164	9163.4	4.623
2150.	29.904	4.370	34.273	9394.6	4.627
2200.	30.004	4.375	34.380	9626.1	4.631
2250.	30.102	4.381	34.484	9857.7	4.635
2300.	30.199	4.387	34.586	10089.6	4.639
2350.	30.293	4.392	34.685	10321.6	4.643
2400.	30.386	4.397	34.783	10553.9	4.647

This table has been computed for the ground state of the molecule, which is taken as $^1\Sigma$, using the following molecular constants: $B_e = 0.7103$ cm^{-1}, $\alpha_e = 0.0062$ cm^{-1}, $D_e = 3.393 \times 10^{-6}$ cm^{-1}, $\omega_e x_e = 4.3$ cm^{-1}, and $\omega_e = 650.0$ cm^{-1}. See reverse side for conversion factors.

Table 3. Thermodynamic Functions for LiCl - Continued

T °K	$\frac{-(F^{\circ}-H_0^{\circ})}{RT}$	$\frac{H^{\circ}-H_0^{\circ}}{RT}$	$\frac{S^{\circ}}{R}$	$\frac{H^{\circ}-H_0^{\circ}}{R}$	$\frac{C_p^{\circ}}{R}$
2450.	30.476	4.403	34.879	10786.3	4.651
2500.	30.565	4.408	34.973	11018.9	4.654
2600.	30.738	4.417	35.156	11484.7	4.662
2700.	30.905	4.426	35.332	11951.3	4.669
2800.	31.067	4.435	35.502	12418.6	4.677
2900.	31.222	4.444	35.666	12886.6	4.684
3000.	31.373	4.452	35.825	13355.4	4.691
3100.	31.519	4.460	35.979	13824.8	4.698
3200.	31.661	4.467	36.128	14295.0	4.705
3300.	31.798	4.475	36.273	14765.9	4.712
3400.	31.932	4.482	36.414	15237.5	4.719
3500.	32.062	4.489	36.551	15709.8	4.726
3600.	32.189	4.495	36.684	16182.7	4.733
3700.	32.312	4.502	36.814	16656.4	4.740
3800.	32.432	4.508	36.940	17130.8	4.747
3900.	32.549	4.514	37.064	17605.9	4.754
4000.	32.664	4.520	37.184	18081.6	4.761
4100.	32.775	4.526	37.302	18558.0	4.768
4200.	32.884	4.532	37.417	19035.2	4.775
4300.	32.991	4.538	37.529	19513.0	4.781
4400.	33.096	4.544	37.639	19991.5	4.788
4500.	33.198	4.549	37.747	20470.6	4.795
4600.	33.298	4.554	37.852	20950.5	4.802
4700.	33.396	4.560	37.956	21431.0	4.809
4800.	33.492	4.565	38.057	21912.2	4.815
4900.	33.586	4.570	38.156	22394.1	4.822
5000.	33.678	4.575	38.254	22876.6	4.829
5100.	33.769	4.580	38.349	23359.9	4.836
5200.	33.858	4.585	38.443	23843.8	4.842
5300.	33.945	4.590	38.536	24328.3	4.849
5400.	34.031	4.595	38.626	24813.6	4.856
5500.	34.116	4.600	38.716	25299.5	4.863
5600.	34.199	4.605	38.803	25786.1	4.869
5700.	34.280	4.609	38.889	26273.4	4.876
5800.	34.360	4.614	38.974	26761.3	4.883
5900.	34.439	4.619	39.058	27249.9	4.889
6000.	34.517	4.623	39.140	27739.2	4.896
273.15	21.612	3.622	25.234	989.3	3.928
298.15	21.930	3.650	25.581	1088.3	3.989

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal mole^{-1} °K^{-1} (or °C^{-1})	1.98726
cal g^{-1} °K^{-1} (or °C^{-1})	0.046873
joules g^{-1} °K^{-1} (or °C^{-1})	0.196115
Btu (lb mole)$^{-1}$ °R^{-1} (or °F^{-1})	1.98595
Btu lb^{-1} °R^{-1} (or °F^{-1})	0.046842

Table 4. Thermodynamic Functions for BeF

T °K	$\frac{-(F^{o}-H^{o}_{0})}{RT}$	$\frac{H^{o}-H^{o}_{0}}{RT}$	$\frac{S^{o}}{R}$	$\frac{H^{o}-H^{o}_{0}}{R}$	$\frac{C^{o}_{p}}{R}$
50.	14.978	3.486	18.464	174.3	3.501
75.	16.393	3.491	19.884	261.8	3.501
100.	17.397	3.493	20.891	349.3	3.501
125.	18.177	3.495	21.672	436.9	3.501
150.	18.814	3.496	22.311	524.4	3.502
175.	19.353	3.497	22.851	612.0	3.506
200.	19.820	3.499	23.319	699.7	3.512
225.	20.233	3.501	23.733	787.7	3.524
250.	20.602	3.504	24.106	876.0	3.542
275.	20.936	3.509	24.444	964.8	3.566
300.	21.241	3.514	24.756	1054.3	3.595
325.	21.523	3.522	25.045	1144.6	3.628
350.	21.784	3.531	25.315	1235.8	3.663
375.	22.028	3.541	25.569	1327.8	3.701
400.	22.257	3.552	25.809	1420.8	3.739
425.	22.473	3.564	26.037	1514.8	3.778
450.	22.677	3.577	26.254	1609.7	3.815
475.	22.871	3.591	26.461	1705.5	3.852
500.	23.055	3.605	26.660	1802.3	3.888
550.	23.400	3.633	27.033	1998.3	3.954
600.	23.717	3.663	27.380	2197.6	4.014
650.	24.012	3.692	27.704	2399.6	4.067
700.	24.286	3.720	28.007	2604.2	4.115
750.	24.544	3.748	28.292	2811.0	4.156
800.	24.787	3.775	28.562	3019.8	4.193
850.	25.016	3.800	28.817	3230.3	4.226
900.	25.234	3.825	29.059	3442.3	4.255
950.	25.442	3.848	29.290	3655.7	4.281
1000.	25.640	3.870	29.510	3870.4	4.304
1050.	25.829	3.892	29.721	4086.1	4.325
1100.	26.011	3.912	29.922	4302.8	4.344
1150.	26.185	3.931	30.116	4520.5	4.361
1200.	26.353	3.949	30.302	4738.9	4.376
1250.	26.514	3.966	30.481	4958.0	4.390
1300.	26.670	3.983	30.653	5177.8	4.403
1350.	26.821	3.999	30.819	5398.3	4.414
1400.	26.966	4.014	30.980	5619.3	4.425
1450.	27.107	4.028	31.136	5840.8	4.435
1500.	27.244	4.042	31.286	6062.8	4.445
1550.	27.377	4.055	31.432	6285.2	4.453
1600.	27.506	4.068	31.573	6508.1	4.461
1650.	27.631	4.080	31.711	6731.4	4.469
1700.	27.753	4.091	31.844	6955.0	4.476
1750.	27.872	4.102	31.974	7179.0	4.483
1800.	27.988	4.113	32.101	7403.3	4.489
1850.	28.101	4.123	32.224	7627.9	4.495
1900.	28.211	4.133	32.344	7852.9	4.501
1950.	28.318	4.143	32.461	8078.1	4.507
2000.	28.423	4.152	32.575	8303.5	4.512
2050.	28.526	4.161	32.686	8529.2	4.517
2100.	28.626	4.169	32.795	8755.2	4.522
2150.	28.724	4.177	32.902	8981.4	4.526
2200.	28.820	4.185	33.006	9207.8	4.531
2250.	28.915	4.193	33.108	9434.5	4.535
2300.	29.007	4.201	33.207	9661.3	4.539
2350.	29.097	4.208	33.305	9888.4	4.543
2400.	29.186	4.215	33.401	10115.7	4.547

This table has been computed for the ground state of the molecule, which is taken as $^{2}\Sigma$, using the following molecular constants: B_e = 1.4877 cm^{-1}, α_e = 0.0168 cm^{-1}, D_e = 8.21 x 10^{-6} cm^{-1}, $\omega_e x_e$ = 9.12 cm^{-1}, and ω_e = 1265.6 cm^{-1}. See reverse side for conversion factors.

Table 4. Thermodynamic Functions for BeF - Continued

T °K	$\frac{-(F^\circ - H^\circ_0)}{RT}$	$\frac{H^\circ - H^\circ_0}{RT}$	$\frac{S^\circ}{R}$	$\frac{H^\circ - H^\circ_0}{R}$	$\frac{C^\circ_p}{R}$
2450.	29.273	4.222	33.495	10343.1	4.55_
2500.	29.358	4.228	33.587	10570.8	4.555
2600.	29.524	4.241	33.765	11026.6	4.562
2700.	29.685	4.253	33.938	11483.1	4.568
2800.	29.839	4.264	34.104	11940.2	4.575
2900.	29.989	4.275	34.264	12398.0	4.581
3000.	30.134	4.285	34.420	12856.4	4.587
3100.	30.275	4.295	34.570	13315.4	4.593
3200.	30.412	4.305	34.716	13775.0	4.598
3300.	30.544	4.314	34.858	14235.1	4.604
3400.	30.673	4.322	34.995	14695.7	4.609
3500.	30.799	4.331	35.129	15156.9	4.614
3600.	30.921	4.338	35.259	15618.6	4.619
3700.	31.040	4.346	35.386	16080.8	4.624
3800.	31.156	4.354	35.509	16543.5	4.629
3900.	31.269	4.361	35.629	17006.7	4.634
4000.	31.379	4.368	35.747	17470.3	4.639
4100.	31.487	4.374	35.861	17934.4	4.644
4200.	31.593	4.381	35.973	18399.0	4.648
4300.	31.696	4.387	36.083	18864.1	4.653
4400.	31.797	4.393	36.190	19329.6	4.658
4500.	31.896	4.399	36.295	19795.6	4.662
4600.	31.992	4.405	36.397	20262.0	4.667
4700.	32.087	4.410	36.498	20728.9	4.671
4800.	32.180	4.416	36.596	21196.2	4.675
4900.	32.271	4.421	36.692	21664.0	4.680
5000.	32.360	4.426	36.787	22132.2	4.684
5100.	32.448	4.432	36.880	22600.8	4.688
5200.	32.534	4.437	36.971	23069.9	4.693
5300.	32.619	4.441	37.060	23539.4	4.697
5400.	32.702	4.446	37.148	24009.3	4.701
5500.	32.784	4.451	37.234	24479.6	4.705
5600.	32.864	4.455	37.319	24950.4	4.710
5700.	32.943	4.460	37.403	25421.5	4.714
5800.	33.020	4.464	37.485	25893.1	4.718
5900.	33.097	4.469	37.565	26365.2	4.722
6000.	33.172	4.473	37.645	26837.6	4.726
273.15	20.912	3.508	24.420	958.2	3.564
298.15	21.220	3.514	24.734	1047.7	3.593

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal mole^{-1} °K^{-1} (or °C^{-1})	1.98726
cal g^{-1} °K^{-1} (or °C^{-1})	0.070941
joules g^{-1} °K^{-1} (or °C^{-1})	0.296816
Btu (lb mole)$^{-1}$ °R^{-1} (or °F^{-1})	1.98595
Btu lb^{-1} °R^{-1} (or °F^{-1})	0.070894

Table 5. Thermodynamic Functions for BeCl

T °K	$\frac{-(F^{\circ}-H_0^{\circ})}{RT}$	$\frac{H^{\circ}-H_0^{\circ}}{RT}$	$\frac{S^{\circ}}{R}$	$\frac{H^{\circ}-H_0^{\circ}}{R}$	$\frac{C_p^{\circ}}{R}$
50.	16.327	3.493	19.820	174.6	3.501
75.	17.744	3.496	21.239	262.2	3.501
100.	18.750	3.497	22.247	349.7	3.502
125.	19.530	3.498	23.029	437.3	3.508
150.	20.168	3.501	23.669	525.2	3.523
175.	20.708	3.506	24.214	613.6	3.551
200.	21.177	3.514	24.691	702.8	3.592
225.	21.591	3.526	25.117	793.2	3.641
250.	21.964	3.540	25.503	885.0	3.696
275.	22.302	3.557	25.858	978.1	3.753
300.	22.612	3.575	26.187	1072.6	3.809
325.	22.899	3.595	26.494	1168.5	3.864
350.	23.166	3.616	26.783	1265.8	3.915
375.	23.416	3.638	27.054	1364.2	3.963
400.	23.652	3.660	27.312	1463.9	4.007
425.	23.874	3.681	27.556	1564.5	4.047
450.	24.085	3.703	27.788	1666.2	4.084
475.	24.286	3.724	28.010	1768.7	4.118
500.	24.478	3.744	28.222	1872.0	4.148
550.	24.836	3.783	28.620	2080.8	4.202
600.	25.167	3.820	28.987	2292.0	4.246
650.	25.474	3.854	29.329	2505.3	4.283
700.	25.761	3.886	29.647	2720.3	4.315
750.	26.030	3.916	29.946	2936.7	4.342
800.	26.284	3.943	30.227	3154.4	4.365
850.	26.524	3.968	30.492	3373.2	4.385
900.	26.751	3.992	30.743	3592.9	4.403
950.	26.968	4.014	30.982	3813.4	4.418
1000.	27.174	4.035	31.209	4034.6	4.432
1050.	27.371	4.054	31.425	4256.5	4.444
1100.	27.560	4.072	31.632	4479.0	4.455
1150.	27.742	4.089	31.830	4702.0	4.465
1200.	27.916	4.105	32.021	4925.5	4.474
1250.	28.084	4.120	32.204	5149.4	4.483
1300.	28.246	4.134	32.379	5373.7	4.490
1350.	28.402	4.147	32.549	5598.4	4.497
1400.	28.553	4.160	32.713	5823.5	4.504
1450.	28.699	4.172	32.871	6048.8	4.510
1500.	28.841	4.183	33.024	6274.5	4.516
1550.	28.978	4.194	33.172	6500.5	4.522
1600.	29.112	4.204	33.316	6726.7	4.527
1650.	29.241	4.214	33.455	6953.2	4.532
1700.	29.367	4.223	33.591	7179.9	4.537
1750.	29.490	4.233	33.722	7406.9	4.542
1800.	29.609	4.241	33.850	7634.1	4.546
1850.	29.725	4.249	33.975	7861.5	4.550
1900.	29.839	4.257	34.096	8089.1	4.554
1950.	29.949	4.265	34.215	8316.9	4.558
2000.	30.058	4.272	34.330	8545.0	4.562
2050.	30.163	4.280	34.443	8773.2	4.566
2100.	30.266	4.286	34.553	9001.6	4.570
2150.	30.367	4.293	34.660	9230.1	4.573
2200.	30.466	4.299	34.765	9458.9	4.577
2250.	30.563	4.306	34.868	9687.8	4.580
2300.	30.657	4.312	34.969	9916.9	4.583
2350.	30.750	4.318	35.068	10146.1	4.587
2400.	30.841	4.323	35.164	10375.6	4.590

This table has been computed for the ground state of the molecule, which is taken as $^2\Sigma$, using the following molecular constants: $B_e = 0.766$ cm^{-1}, $\alpha_e = 0.007$ cm^{-1}, $D_e = 2.5 \times 10^{-6}$ cm^{-1}, $\omega_e x_e = 5.11$ cm^{-1}, and $\omega_e = 846.6$ cm^{-1}. See reverse side for conversion factors.

Table 5. Thermodynamic Functions for BeCl - Continued

T °K	$\frac{-(F^{\circ}-H_0^{\circ})}{RT}$	$\frac{H^{\circ}-H_0^{\circ}}{RT}$	$\frac{S^{\circ}}{R}$	$\frac{H^{\circ}-H_0^{\circ}}{R}$	$\frac{C_p^{\circ}}{R}$
2450.	30.930	4.329	35.259	10605.1	4.593
2500.	31.018	4.334	35.352	10834.9	4.596
2600.	31.188	4.344	35.532	11294.8	4.602
2700.	31.352	4.354	35.706	11755.3	4.608
2800.	31.511	4.363	35.874	12216.4	4.614
2900.	31.664	4.372	36.036	12678.1	4.620
3000.	31.812	4.380	36.192	13140.3	4.625
3100.	31.956	4.388	36.344	13603.1	4.631
3200.	32.095	4.396	36.491	14066.5	4.636
3300.	32.231	4.403	36.634	14530.4	4.641
3400.	32.362	4.410	36.773	14994.8	4.647
3500.	32.490	4.417	36.907	15459.7	4.652
3600.	32.615	4.424	37.039	15925.2	4.657
3700.	32.736	4.430	37.166	16391.1	4.662
3800.	32.854	4.436	37.291	16857.6	4.667
3900.	32.970	4.442	37.412	17324.6	4.672
4000.	33.082	4.448	37.530	17792.1	4.677
4100.	33.192	4.454	37.646	18260.1	4.682
4200.	33.300	4.459	37.759	18728.6	4.687
4300.	33.405	4.465	37.869	19197.6	4.692
4400.	33.507	4.470	37.977	19667.1	4.697
4500.	33.608	4.475	38.083	20137.0	4.702
4600.	33.706	4.480	38.186	20607.5	4.707
4700.	33.803	4.485	38.287	21078.4	4.712
4800.	33.897	4.490	38.387	21549.9	4.717
4900.	33.990	4.494	38.484	22021.8	4.722
5000.	34.080	4.499	38.579	22494.2	4.726
5100.	34.170	4.503	38.673	22967.1	4.731
5200.	34.257	4.508	38.765	23440.5	4.736
5300.	34.343	4.512	38.855	23914.3	4.741
5400.	34.427	4.516	38.944	24388.6	4.746
5500.	34.510	4.521	39.031	24863.5	4.750
5600.	34.592	4.525	39.117	25338.7	4.755
5700.	34.672	4.529	39.201	25814.5	4.760
5800.	34.751	4.533	39.284	26290.7	4.765
5900.	34.828	4.537	39.365	26767.5	4.770
6000.	34.905	4.541	39.445	27244.6	4.774
273.15	22.278	3.555	25.833	971.1	3.749
298.15	22.590	3.574	26.164	1065.6	3.805

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal mole^{-1} °K^{-1} (or °C^{-1})	1.98726
cal g^{-1} °K^{-1} (or °C^{-1})	0.44688
joules g^{-1} °K^{-1} (or °C^{-1})	0.186973
Btu (lb mole)$^{-1}$ °R^{-1} (or °F^{-1})	1.98595
Btu lb^{-1} °R^{-1} (or °F^{-1})	0.044658

Table 6. Thermodynamic Functions for BeO

T °K	$\frac{-(F^{\circ}-H_0^{\circ})}{RT}$	$\frac{H^{\circ}-H_0^{\circ}}{RT}$	$\frac{S^{\circ}}{R}$	$\frac{H^{\circ}-H_0^{\circ}}{R}$	$\frac{C_p^{\circ}}{R}$
50.	14.013	3.484	17.497	174.2	3.500
75.	15.427	3.490	18.916	261.7	3.501
100.	16.431	3.493	19.923	349.3	3.501
125.	17.210	3.494	20.705	436.8	3.501
150.	17.848	3.495	21.343	524.3	3.501
175.	18.387	3.496	21.883	611.9	3.502
200.	18.853	3.497	22.351	699.4	3.505
225.	19.265	3.498	22.764	787.1	3.510
250.	19.634	3.500	23.134	874.9	3.518
275.	19.968	3.502	23.470	963.0	3.530
300.	20.273	3.505	23.778	1051.5	3.547
325.	20.553	3.509	24.062	1140.4	3.568
350.	20.814	3.514	24.328	1229.9	3.593
375.	21.056	3.520	24.576	1320.1	3.620
400.	21.284	3.527	24.811	1411.0	3.650
425.	21.498	3.536	25.033	1502.6	3.681
450.	21.700	3.545	25.245	1595.0	3.714
475.	21.892	3.554	25.446	1688.3	3.746
500.	22.074	3.565	25.639	1782.4	3.779
550.	22.415	3.587	26.002	1972.9	3.843
600.	22.728	3.611	26.339	2166.6	3.903
650.	23.018	3.636	26.654	2363.2	3.959
700.	23.289	3.661	26.949	2562.4	4.010
750.	23.542	3.685	27.228	2764.1	4.057
800.	23.781	3.710	27.491	2968.0	4.098
850.	24.006	3.734	27.740	3173.9	4.136
900.	24.221	3.757	27.978	3381.5	4.170
950.	24.424	3.780	28.204	3590.8	4.200
1000.	24.619	3.802	28.420	3801.5	4.228
1050.	24.805	3.822	28.627	4013.6	4.253
1100.	24.983	3.843	28.826	4226.8	4.276
1150.	25.154	3.862	29.016	4441.1	4.296
1200.	25.319	3.880	29.199	4656.4	4.315
1250.	25.478	3.898	29.376	4872.5	4.332
1300.	25.631	3.915	29.546	5089.5	4.347
1350.	25.779	3.931	29.710	5307.3	4.362
1400.	25.922	3.947	29.869	5525.7	4.375
1450.	26.061	3.962	30.023	5744.7	4.387
1500.	26.196	3.976	30.172	5964.4	4.399
1550.	26.326	3.990	30.316	6184.6	4.409
1600.	26.453	4.003	30.456	6405.3	4.419
1650.	26.576	4.016	30.593	6626.5	4.428
1700.	26.697	4.028	30.725	6848.1	4.437
1750.	26.814	4.040	30.854	7070.1	4.445
1800.	26.927	4.051	30.979	7292.6	4.452
1850.	27.039	4.062	31.101	7515.3	4.460
1900.	27.147	4.073	31.220	7738.5	4.466
1950.	27.253	4.083	31.336	7962.0	4.473
2000.	27.357	4.093	31.449	8185.8	4.479
2050.	27.458	4.102	31.560	8409.9	4.485
2100.	27.557	4.112	31.668	8634.2	4.490
2150.	27.654	4.120	31.774	8858.9	4.495
2200.	27.748	4.129	31.877	9083.8	4.501
2250.	27.841	4.137	31.979	9308.9	4.505
2300.	27.932	4.145	32.078	9534.3	4.510
2350.	28.021	4.153	32.175	9759.9	4.515
2400.	28.109	4.161	32.270	9985.8	4.519

This table has been computed for the ground state of the molecule, which is taken as $^1\Sigma$, using the following molecular constants: $B_e = 1.6510$ cm^{-1}, $\alpha_e = 0.0190$ cm^{-1}, $D_e = 8.198 \times 10^{-6}$ cm^{-1}, $\omega_e x_e = 11.731$ cm^{-1}, and $\omega_e = 1487.19$ cm^{-1}. See reverse side for conversion factors.

Table 6. Thermodynamic Functions for BeO - Continued

T °K	$\frac{-(F^{\circ}-H_0^{\circ})}{RT}$	$\frac{H^{\circ}-H_0^{\circ}}{RT}$	$\frac{S^{\circ}}{R}$	$\frac{H^{\circ}-H_0^{\circ}}{R}$	$\frac{C_p^{\circ}}{R}$
2450.	28.195	4.168	32.363	10211.8	4.523
2500.	28.279	4.175	32.454	10438.1	4.527
2600.	28.443	4.189	32.632	10891.2	4.535
2700.	28.602	4.202	32.803	11345.0	4.542
2800.	28.755	4.214	32.969	11799.6	4.549
2900.	28.903	4.226	33.128	12254.8	4.556
3000.	29.046	4.237	33.283	12710.7	4.562
3100.	29.185	4.247	33.433	13167.1	4.568
3200.	29.320	4.258	33.578	13624.2	4.573
3300.	29.451	4.267	33.719	14081.8	4.579
3400.	29.579	4.276	33.855	14540.0	4.584
3500.	29.703	4.285	33.988	14998.7	4.590
3600.	29.824	4.294	34.118	15457.9	4.595
3700.	29.942	4.302	34.244	15917.6	4.600
3800.	30.056	4.310	34.366	16377.9	4.604
3900.	30.168	4.318	34.486	16838.5	4.609
4000.	30.278	4.325	34.603	17299.7	4.614
4100.	30.385	4.332	34.717	17761.3	4.618
4200.	30.489	4.339	34.828	18223.4	4.623
4300.	30.591	4.346	34.937	18685.9	4.627
4400.	30.691	4.352	35.043	19148.8	4.632
4500.	30.789	4.358	35.148	19612.2	4.636
4600.	30.885	4.364	35.249	20076.0	4.640
4700.	30.979	4.370	35.349	20540.2	4.644
4800.	31.071	4.376	35.447	21004.8	4.648
4900.	31.161	4.382	35.543	21469.9	4.652
5000.	31.250	4.387	35.637	21935.3	4.657
5100.	31.337	4.392	35.729	22401.2	4.661
5200.	31.422	4.398	35.820	22867.4	4.665
5300.	31.506	4.403	35.909	23334.1	4.668
5400.	31.588	4.408	35.996	23801.1	4.672
5500.	31.669	4.412	36.082	24268.5	4.676
5600.	31.749	4.417	36.166	24736.4	4.680
5700.	31.827	4.422	36.249	25204.6	4.684
5800.	31.904	4.426	36.330	25673.2	4.688
5900.	31.980	4.431	36.411	26142.1	4.692
6000.	32.054	4.435	36.489	26611.5	4.695
273.15	19.944	3.502	23.446	956.5	3.529
298.15	20.251	3.505	23.756	1044.9	3.546

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal $mole^{-1}$ $°K^{-1}$ (or $°C^{-1}$)	1.98726
cal g^{-1} $°K^{-1}$ (or $°C^{-1}$)	0.079449
joules g^{-1} $°K^{-1}$ (or $°C^{-1}$)	0.332415
Btu $(lb\ mole)^{-1}$ $°R^{-1}$ (or $°F^{-1}$)	1.98595
Btu lb^{-1} $°R^{-1}$ (or $°F^{-1}$)	0.079397

Table 7. Thermodynamic Functions for MgF

T °K	$\frac{-(F^o-H_0^o)}{RT}$	$\frac{H^o-H_0^o}{RT}$	$\frac{S^o}{R}$	$\frac{H^o-H_0^o}{R}$	$\frac{C_p^o}{R}$
50.	16.680	3.495	20.175	174.8	3.501
75.	18.097	3.497	21.595	262.3	3.501
100.	19.104	3.498	22.602	349.8	3.505
125.	19.885	3.501	23.386	437.6	3.521
150.	20.523	3.507	24.030	526.0	3.554
175.	21.065	3.517	24.582	615.5	3.603
200.	21.535	3.531	25.067	706.3	3.664
225.	21.952	3.550	25.502	798.7	3.730
250.	22.327	3.571	25.898	892.8	3.797
275.	22.669	3.595	26.263	988.5	3.861
300.	22.982	3.619	26.602	1085.8	3.921
325.	23.273	3.645	26.918	1184.5	3.976
350.	23.544	3.670	27.214	1284.5	4.026
375.	23.798	3.695	27.494	1385.7	4.071
400.	24.038	3.720	27.758	1488.0	4.111
425.	24.264	3.744	28.008	1591.3	4.147
450.	24.478	3.767	28.246	1695.3	4.179
475.	24.683	3.790	28.473	1800.2	4.208
500.	24.878	3.811	28.689	1905.7	4.234
550.	25.243	3.852	29.095	2118.6	4.279
600.	25.580	3.889	29.469	2333.5	4.315
650.	25.892	3.923	29.815	2550.0	4.345
700.	26.184	3.954	30.138	2767.9	4.370
750.	26.458	3.983	30.441	2987.0	4.392
800.	26.716	4.009	30.725	3207.0	4.410
850.	26.960	4.033	30.993	3427.9	4.426
900.	27.191	4.055	31.246	3649.6	4.440
950.	27.411	4.076	31.486	3871.9	4.452
1000.	27.620	4.095	31.715	4094.8	4.463
1050.	27.820	4.113	31.933	4318.2	4.473
1100.	28.012	4.129	32.141	4542.0	4.482
1150.	28.196	4.145	32.341	4766.3	4.490
1200.	28.373	4.159	32.532	4991.0	4.497
1250.	28.543	4.173	32.716	5216.0	4.504
1300.	28.707	4.186	32.892	5441.4	4.510
1350.	28.865	4.198	33.063	5667.1	4.516
1400.	29.018	4.209	33.227	5893.0	4.522
1450.	29.166	4.220	33.386	6119.2	4.527
1500.	29.309	4.230	33.539	6345.7	4.532
1550.	29.448	4.240	33.688	6572.4	4.537
1600.	29.583	4.250	33.832	6799.4	4.541
1650.	29.713	4.259	33.972	7026.5	4.546
1700.	29.841	4.267	34.108	7253.9	4.550
1750.	29.964	4.275	34.240	7481.5	4.554
1800.	30.085	4.283	34.368	7709.3	4.558
1850.	30.202	4.290	34.493	7937.3	4.561
1900.	30.317	4.298	34.615	8165.4	4.565
1950.	30.429	4.305	34.733	8393.8	4.569
2000.	30.538	4.311	34.849	8622.3	4.572
2050.	30.644	4.318	34.962	8851.0	4.575
2100.	30.748	4.324	35.072	9079.8	4.579
2150.	30.850	4.330	35.180	9308.9	4.582
2200.	30.950	4.335	35.285	9538.0	4.585
2250.	31.047	4.341	35.388	9767.4	4.588
2300.	31.143	4.346	35.489	9996.9	4.591
2350.	31.236	4.352	35.588	10226.5	4.594
2400.	31.328	4.357	35.685	10456.3	4.597

This table has been computed for the ground state of the molecule, which is taken as $^2\Sigma$, using the following molecular constants: B_e = 0.516 cm^{-1}, α_e = 0.004 cm^{-1}, D_e = 1.1×10^{-6} cm^{-1}, $\omega_e x_e$ = 3.84 cm^{-1}, and ω_e = 717.0 cm^{-1}. See reverse side for conversion factors.

Table 7. Thermodynamic Functions for MgF - Continued

T °K	$\frac{-(F^{\circ}-H^{\circ}_0)}{RT}$	$\frac{H^{\circ}-H^{\circ}_0}{RT}$	$\frac{S^{\circ}}{R}$	$\frac{H^{\circ}-H^{\circ}_0}{R}$	$\frac{C^{\circ}_p}{R}$
2450.	31.418	4.362	35.780	10686.3	4.600
2500.	31.506	4.367	35.873	10916.4	4.603
2600.	31.678	4.376	36.053	11377.0	4.609
2700.	31.843	4.385	36.227	11838.2	4.615
2800.	32.002	4.393	36.395	12299.9	4.620
2900.	32.157	4.401	36.557	12762.2	4.626
3000.	32.306	4.408	36.714	13225.1	4.631
3100.	32.451	4.416	36.866	13688.4	4.636
3200.	32.591	4.423	37.014	14152.3	4.642
3300.	32.727	4.429	37.157	14616.8	4.647
3400.	32.860	4.436	37.295	15081.7	4.652
3500.	32.988	4.442	37.430	15547.2	4.657
3600.	33.113	4.448	37.562	16013.1	4.662
3700.	33.235	4.454	37.689	16479.6	4.667
3800.	33.354	4.460	37.814	16946.6	4.672
3900.	33.470	4.465	37.935	17414.1	4.677
4000.	33.583	4.471	38.054	17882.0	4.682
4100.	33.694	4.476	38.169	18350.5	4.687
4200.	33.802	4.481	38.282	18819.5	4.692
4300.	33.907	4.486	38.393	19289.0	4.697
4400.	34.010	4.491	38.501	19758.9	4.702
4500.	34.111	4.495	38.607	20229.4	4.707
4600.	34.210	4.500	38.710	20700.3	4.712
4700.	34.307	4.505	38.812	21171.7	4.717
4800.	34.402	4.509	38.911	21643.6	4.722
4900.	34.495	4.513	39.008	22116.0	4.726
5000.	34.586	4.518	39.104	22588.9	4.731
5100.	34.676	4.522	39.198	23062.3	4.736
5200.	34.763	4.526	39.290	23536.1	4.741
5300.	34.850	4.530	39.380	24010.4	4.746
5400.	34.934	4.534	39.469	24485.3	4.751
5500.	35.018	4.538	39.556	24960.5	4.755
5600.	35.099	4.542	39.642	25436.3	4.760
5700.	35.180	4.546	39.726	25912.6	4.765
5800.	35.259	4.550	39.809	26389.3	4.770
5900.	35.337	4.554	39.890	26866.5	4.774
6000.	35.413	4.557	39.971	27344.2	4.779
273.15	22.644	3.593	26.237	981.4	3.856
298.15	22.960	3.617	26.577	1078.5	3.917

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal $mole^{-1}$ $°K^{-1}$ (or $°C^{-1}$)	1.98726
cal g^{-1} $°K^{-1}$ (or $°C^{-1}$)	0.045874
joules g^{-1} $°K^{-1}$ (or $°C^{-1}$)	0.191937
Btu $(lb\ mole)^{-1}$ $°R^{-1}$ (or $°F^{-1}$)	1.98595
Btu lb^{-1} $°R^{-1}$ (or $°F^{-1}$)	0.045844

Table 8. Thermodynamic Functions for MgCl

T °K	$\frac{-(F^{\circ}-H_0^{\circ})}{RT}$	$\frac{H^{\circ}-H_0^{\circ}}{RT}$	$\frac{S^{\circ}}{R}$	$\frac{H^{\circ}-H_0^{\circ}}{R}$	$\frac{C_p^{\circ}}{R}$
50.	17.904	3.498	21.402	174.9	3.501
75.	19.323	3.500	22.823	262.5	3.512
100.	20.331	3.508	23.839	350.8	3.559
125.	21.115	3.526	24.642	440.8	3.643
150.	21.761	3.554	25.315	533.1	3.744
175.	22.311	3.588	25.899	628.0	3.844
200.	22.793	3.626	26.419	725.2	3.936
225.	23.222	3.665	26.887	824.7	4.015
250.	23.610	3.704	27.314	925.9	4.083
275.	23.965	3.741	27.706	1028.7	4.140
300.	24.292	3.776	28.068	1132.9	4.189
325.	24.596	3.810	28.405	1238.1	4.229
350.	24.879	3.841	28.720	1344.3	4.264
375.	25.145	3.870	29.015	1451.3	4.294
400.	25.396	3.897	29.293	1558.9	4.319
425.	25.633	3.923	29.555	1667.2	4.341
450.	25.858	3.947	29.804	1775.9	4.360
475.	26.072	3.969	30.040	1885.2	4.377
500.	26.276	3.990	30.265	1994.8	4.391
550.	26.658	4.027	30.685	2215.0	4.416
600.	27.010	4.061	31.070	2436.3	4.436
650.	27.336	4.090	31.426	2658.5	4.453
700.	27.640	4.116	31.756	2881.5	4.467
750.	27.925	4.140	32.065	3105.2	4.478
800.	28.193	4.162	32.354	3329.3	4.489
850.	28.446	4.181	32.627	3554.0	4.498
900.	28.685	4.199	32.884	3779.1	4.506
950.	28.912	4.215	33.128	4004.6	4.513
1000.	29.129	4.230	33.359	4230.4	4.520
1050.	29.336	4.244	33.580	4456.5	4.526
1100.	29.534	4.257	33.791	4682.9	4.531
1150.	29.723	4.269	33.992	4909.6	4.537
1200.	29.905	4.281	34.186	5136.6	4.542
1250.	30.080	4.291	34.371	5363.8	4.547
1300.	30.248	4.301	34.549	5591.3	4.551
1350.	30.411	4.310	34.721	5818.9	4.556
1400.	30.568	4.319	34.887	6046.8	4.560
1450.	30.720	4.328	35.047	6274.9	4.564
1500.	30.866	4.335	35.202	6503.2	4.568
1550.	31.009	4.343	35.352	6731.7	4.572
1600.	31.147	4.350	35.497	6960.4	4.575
1650.	31.281	4.357	35.638	7189.2	4.579
1700.	31.411	4.364	35.775	7418.3	4.583
1750.	31.537	4.370	35.907	7647.5	4.586
1800.	31.661	4.376	36.037	7876.9	4.590
1850.	31.781	4.382	36.162	8106.4	4.593
1900.	31.898	4.387	36.285	8336.2	4.596
1950.	32.012	4.393	36.404	8566.1	4.600
2000.	32.123	4.398	36.521	8796.1	4.603
2050.	32.232	4.403	36.635	9026.4	4.606
2100.	32.338	4.408	36.746	9256.8	4.609
2150.	32.441	4.413	36.854	9487.3	4.613
2200.	32.543	4.417	36.960	9718.0	4.616
2250.	32.642	4.422	37.064	9948.9	4.619
2300.	32.740	4.426	37.166	10179.9	4.622
2350.	32.835	4.430	37.265	10411.1	4.625
2400.	32.928	4.434	37.362	10642.4	4.628

This table has been computed for the ground state of the molecule, which is taken as $^2\Sigma$, using the following molecular constants: $B_e{}' = 0.245 \text{ cm}^{-1}$, $\alpha_e = 0.001 \text{ cm}^{-1}$, $D_e = 0.25 \times 10^{-6} \text{ cm}^{-1}$, $\omega_e x_e = 2.05 \text{ cm}^{-1}$, and $\omega_e = 465.4 \text{ cm}^{-1}$. See reverse side for conversion factors.

Table 8. Thermodynamic Functions for MgCl - Continued

T °K	$\frac{-(F^\circ - H^\circ_0)}{RT}$	$\frac{H^\circ - H^\circ_0}{RT}$	$\frac{S^\circ}{R}$	$\frac{H^\circ - H^\circ_0}{R}$	$\frac{C^\circ_p}{R}$
2450.	33.020	4.438	37.458	10873.9	4.631
2500.	33.109	4.442	37.551	11105.5	4.634
2600.	33.284	4.450	37.733	11569.3	4.640
2700.	33.452	4.457	37.909	12033.6	4.646
2800.	33.614	4.464	38.078	12498.6	4.652
2900.	33.771	4.470	38.241	12964.1	4.658
3000.	33.922	4.477	38.399	13430.2	4.664
3100.	34.069	4.483	38.552	13896.9	4.670
3200.	34.212	4.489	38.700	14364.2	4.676
3300.	34.350	4.495	38.844	14832.1	4.682
3400.	34.484	4.500	38.984	15300.6	4.688
3500.	34.615	4.506	39.120	15769.6	4.693
3600.	34.742	4.511	39.253	16239.3	4.699
3700.	34.865	4.516	39.381	16709.5	4.705
3800.	34.986	4.521	39.507	17180.3	4.711
3900.	35.103	4.526	39.629	17651.6	4.716
4000.	35.218	4.531	39.749	18123.5	4.722
4100.	35.330	4.536	39.866	18596.0	4.728
4200.	35.439	4.540	39.980	19069.1	4.734
4300.	35.546	4.545	40.091	19542.8	4.739
4400.	35.651	4.549	40.200	20017.0	4.745
4500.	35.753	4.554	40.307	20491.7	4.751
4600.	35.853	4.558	40.411	20967.1	4.756
4700.	35.951	4.562	40.514	21443.0	4.762
4800.	36.047	4.567	40.614	21919.5	4.768
4900.	36.141	4.571	40.712	22396.6	4.773
5000.	36.234	4.575	40.809	22874.2	4.779
5100.	36.324	4.579	40.903	23352.4	4.785
5200.	36.413	4.583	40.996	23831.2	4.790
5300.	36.501	4.587	41.088	24310.5	4.796
5400.	36.587	4.591	41.177	24790.4	4.802
5500.	36.671	4.595	41.266	25270.8	4.807
5600.	36.754	4.599	41.352	25751.9	4.813
5700.	36.835	4.602	41.437	26233.4	4.819
5800.	36.915	4.606	41.521	26715.6	4.824
5900.	36.994	4.610	41.604	27198.3	4.830
6000.	37.071	4.614	41.685	27681.6	4.836
273.15	23.940	3.738	27.678	1021.1	4.136
298.15	24.269	3.774	28.042	1125.1	4.185

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal mole^{-1} °K^{-1} (or °C^{-1})	1.98726
cal g^{-1} °K^{-1} (or °C^{-1})	0.033245
joules g^{-1} °K^{-1} (or °C^{-1})	0.139095
Btu (lb mole)$^{-1}$ °R^{-1} (or °F^{-1})	1.98595
Btu lb^{-1} °R^{-1} (or °F^{-1})	0.033223

Table 9. Thermodynamic Functions for MgO

T °K	$\frac{-(F^{\circ}-H_0^{\circ})}{RT}$	$\frac{H^{\circ}-H_0^{\circ}}{RT}$	$\frac{S^{\circ}}{R}$	$\frac{H^{\circ}-H_0^{\circ}}{R}$	$\frac{C_p^{\circ}}{R}$
50.	15.773	3.495	19.268	174.7	3.501
75.	17.191	3.497	20.687	262.3	3.501
100.	18.197	3.498	21.695	349.8	3.503
125.	18.977	3.500	22.477	437.5	3.512
150.	19.616	3.503	23.119	525.5	3.535
175.	20.156	3.510	23.667	614.3	3.572
200.	20.626	3.521	24.147	704.2	3.622
225.	21.041	3.535	24.577	795.5	3.680
250.	21.415	3.553	24.968	888.2	3.741
275.	21.754	3.573	25.327	982.5	3.802
300.	22.066	3.594	25.660	1078.3	3.861
325.	22.355	3.617	25.972	1175.5	3.916
350.	22.623	3.640	26.264	1274.1	3.967
375.	22.875	3.664	26.539	1373.9	4.014
400.	23.113	3.687	26.799	1474.8	4.057
425.	23.337	3.710	27.047	1576.7	4.096
450.	23.549	3.732	27.282	1679.5	4.131
475.	23.752	3.754	27.506	1783.2	4.162
500.	23.945	3.775	27.720	1887.6	4.191
550.	24.307	3.815	28.122	2098.4	4.240
600.	24.640	3.853	28.493	2311.5	4.281
650.	24.950	3.887	28.837	2526.4	4.315
700.	25.239	3.919	29.158	2743.0	4.344
750.	25.511	3.948	29.458	2960.8	4.369
800.	25.766	3.975	29.741	3179.8	4.390
850.	26.008	4.000	30.008	3399.7	4.408
900.	26.237	4.023	30.260	3620.5	4.424
950.	26.455	4.044	30.500	3842.0	4.438
1000.	26.663	4.064	30.727	4064.2	4.450
1050.	26.862	4.083	30.945	4287.0	4.461
1100.	27.052	4.100	31.153	4510.4	4.472
1150.	27.235	4.117	31.352	4734.2	4.481
1200.	27.411	4.132	31.543	4958.4	4.489
1250.	27.579	4.146	31.726	5183.1	4.497
1300.	27.742	4.160	31.902	5408.1	4.504
1350.	27.900	4.173	32.073	5633.5	4.511
1400.	28.052	4.185	32.237	5859.2	4.517
1450.	28.199	4.197	32.395	6085.2	4.523
1500.	28.341	4.208	32.549	6311.5	4.529
1550.	28.479	4.218	32.697	6538.1	4.534
1600.	28.613	4.228	32.841	6764.9	4.539
1650.	28.744	4.238	32.981	6992.0	4.544
1700.	28.870	4.247	33.117	7219.3	4.549
1750.	28.993	4.255	33.249	7446.8	4.553
1800.	29.113	4.264	33.377	7674.6	4.557
1850.	29.230	4.272	33.502	7902.6	4.562
1900.	29.344	4.279	33.624	8130.8	4.566
1950.	29.456	4.287	33.742	8359.1	4.570
2000.	29.564	4.294	33.858	8587.7	4.573
2050.	29.670	4.301	33.971	8816.5	4.577
2100.	29.774	4.307	34.081	9045.4	4.581
2150.	29.876	4.314	34.189	9274.5	4.584
2200.	29.975	4.320	34.295	9503.8	4.588
2250.	30.072	4.326	34.398	9733.3	4.591
2300.	30.167	4.332	34.499	9962.9	4.595
2350.	30.260	4.337	34.598	10192.8	4.598
2400.	30.352	4.343	34.694	10422.7	4.601

This table has been computed for the ground state of the molecule, which is taken as $^1\Sigma$, using the following molecular constants: B_e = 0.5743 cm^{-1}, α_e = 0.005 cm^{-1}, D_e = 1.22 x 10^{-6} cm^{-1}, $\omega_e x_e$ = 5.18 cm^{-1}, and ω_e = 785.06 cm^{-1}. See reverse side for conversion factors.

Table 9. Thermodynamic Functions for MgO - Continued

T °K	$\frac{-(F^{\circ}-H_0^{\circ})}{RT}$	$\frac{H^{\circ}-H_0^{\circ}}{RT}$	$\frac{S^{\circ}}{R}$	$\frac{H^{\circ}-H_0^{\circ}}{R}$	$\frac{C_p^{\circ}}{R}$
2450.	30.441	4.348	34.789	10652.9	4.604
2500.	30.529	4.353	34.882	10883.2	4.607
2600.	30.700	4.363	35.063	11344.2	4.614
2700.	30.865	4.373	35.237	11805.9	4.620
2800.	31.024	4.381	35.406	12268.2	4.626
2900.	31.178	4.390	35.568	12731.0	4.632
3000.	31.327	4.398	35.725	13194.5	4.637
3100.	31.471	4.406	35.877	13658.5	4.643
3200.	31.611	4.413	36.025	14123.1	4.649
3300.	31.747	4.421	36.168	14588.3	4.654
3400.	31.879	4.428	36.307	15054.0	4.660
3500.	32.008	4.434	36.442	15520.3	4.665
3600.	32.133	4.441	36.574	15987.1	4.671
3700.	32.255	4.447	36.702	16454.4	4.676
3800.	32.373	4.453	36.826	16922.3	4.682
3900.	32.489	4.459	36.948	17390.7	4.687
4000.	32.602	4.465	37.067	17859.7	4.692
4100.	32.712	4.471	37.183	18329.2	4.698
4200.	32.820	4.476	37.296	18799.2	4.703
4300.	32.925	4.481	37.407	19269.7	4.708
4400.	33.029	4.487	37.515	19740.8	4.713
4500.	33.129	4.492	37.621	20212.4	4.718
4600.	33.228	4.497	37.725	20684.5	4.724
4700.	33.325	4.502	37.826	21157.1	4.729
4800.	33.420	4.506	37.926	21630.3	4.734
4900.	33.513	4.511	38.024	22103.9	4.739
5000.	33.604	4.516	38.120	22578.1	4.744
5100.	33.693	4.520	38.214	23052.8	4.749
5200.	33.781	4.525	38.306	23528.0	4.755
5300.	33.867	4.529	38.396	24003.7	4.760
5400.	33.952	4.533	38.485	24479.9	4.765
5500.	34.035	4.538	38.573	24956.7	4.770
5600.	34.117	4.542	38.659	25433.9	4.775
5700.	34.198	4.546	38.743	25911.7	4.780
5800.	34.277	4.550	38.827	26389.9	4.785
5900.	34.354	4.554	38.908	26868.7	4.790
6000.	34.431	4.558	38.989	27348.0	4.795
273.15	21.730	3.571	25.301	975.5	3.797
298.15	22.044	3.593	25.636	1071.2	3.856

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal mole^{-1} °K^{-1} (or °C^{-1})	1.98726
cal g^{-1} °K^{-1} (or °C^{-1})	0.049287
joules g^{-1} °K^{-1} (or °C^{-1})	0.206218
Btu (lb mole)$^{-1}$ °R^{-1} (or °F^{-1})	1.98595
Btu lb^{-1} °R^{-1} (or °F^{-1})	0.049255

Table 10. Thermodynamic Functions for AlF

T °K	$\frac{-(F^\circ - H_0^\circ)}{RT}$	$\frac{H^\circ - H_0^\circ}{RT}$	$\frac{S^\circ}{R}$	$\frac{H^\circ - H_0^\circ}{R}$	$\frac{C_p^\circ}{R}$
50.	16.009	3.495	19.504	174.7	3.500
75.	17.426	3.497	20.923	262.3	3.501
100.	18.433	3.498	21.931	349.8	3.502
125.	19.213	3.499	22.713	437.4	3.510
150.	19.852	3.503	23.354	525.4	3.531
175.	20.392	3.509	23.901	614.1	3.566
200.	20.861	3.519	24.380	703.8	3.613
225.	21.276	3.532	24.809	794.8	3.668
250.	21.649	3.549	25.198	887.2	3.727
275.	21.988	3.568	25.556	981.2	3.787
300.	22.300	3.589	25.888	1076.6	3.846
325.	22.588	3.611	26.198	1173.4	3.901
350.	22.856	3.633	26.489	1271.6	3.952
375.	23.108	3.656	26.764	1371.0	3.999
400.	23.344	3.679	27.023	1471.5	4.042
425.	23.568	3.701	27.269	1573.0	4.081
450.	23.780	3.723	27.504	1675.5	4.117
475.	23.982	3.745	27.727	1778.8	4.149
500.	24.175	3.766	27.941	1882.9	4.178
550.	24.536	3.806	28.341	2093.1	4.228
600.	24.868	3.843	28.711	2305.6	4.270
650.	25.177	3.877	29.054	2520.0	4.305
700.	25.466	3.909	29.374	2736.0	4.334
750.	25.736	3.938	29.674	2953.3	4.359
800.	25.991	3.965	29.956	3171.8	4.380
850.	26.233	3.990	30.222	3391.3	4.399
900.	26.461	4.013	30.474	3611.6	4.415
950.	26.679	4.034	30.713	3832.7	4.429
1000.	26.886	4.054	30.941	4054.5	4.442
1050.	27.085	4.073	31.158	4276.8	4.453
1100.	27.274	4.091	31.365	4499.7	4.463
1150.	27.457	4.107	31.564	4723.1	4.472
1200.	27.632	4.122	31.754	4947.0	4.481
1250.	27.800	4.137	31.937	5171.2	4.489
1300.	27.963	4.151	32.114	5395.8	4.496
1350.	28.120	4.164	32.283	5620.7	4.502
1400.	28.271	4.176	32.447	5846.0	4.508
1450.	28.418	4.187	32.605	6071.6	4.514
1500.	28.560	4.198	32.759	6297.4	4.520
1550.	28.698	4.209	32.907	6523.6	4.525
1600.	28.832	4.219	33.051	6749.9	4.530
1650.	28.962	4.228	33.190	6976.6	4.535
1700.	29.088	4.237	33.326	7203.4	4.539
1750.	29.211	4.246	33.457	7430.5	4.543
1800.	29.331	4.254	33.585	7657.7	4.548
1850.	29.448	4.262	33.710	7885.2	4.552
1900.	29.561	4.270	33.831	8112.9	4.555
1950.	29.672	4.277	33.950	8340.7	4.559
2000.	29.781	4.284	34.065	8568.8	4.563
2050.	29.887	4.291	34.178	8797.0	4.566
2100.	29.990	4.298	34.288	9025.4	4.570
2150.	30.091	4.304	34.396	9254.0	4.573
2200.	30.190	4.310	34.501	9482.7	4.576
2250.	30.287	4.316	34.604	9711.6	4.580
2300.	30.382	4.322	34.704	9940.7	4.583
2350.	30.475	4.328	34.803	10169.9	4.586
2400.	30.566	4.333	34.899	10399.3	4.589

This table has been computed for the ground state of the molecule, which is taken as $^1\Sigma$, using the following molecular constants: B_e = 0.5523 cm^{-1}, α_e = 0.0048 cm^{-1}, D_e = 0.97 x 10^{-6} cm^{-1}, $\omega_e x_e$ = 4.75 cm^{-1}, and ω_e = 801.0 cm^{-1}. See reverse side for conversion factors.

Table 10. Thermodynamic Functions for AlF - Continued

T °K	$\frac{-(F^o-H^o_0)}{RT}$	$\frac{H^o-H^o_0}{RT}$	$\frac{S^o}{R}$	$\frac{H^o-H^o_0}{R}$	$\frac{C^o_p}{R}$
2450.	30.656	4.338	34.994	10628.8	4.592
2500.	30.744	4.343	35.087	10858.5	4.595
2600.	30.914	4.353	35.267	11318.3	4.601
2700.	31.079	4.362	35.441	11778.6	4.606
2800.	31.237	4.371	35.609	12239.5	4.612
2900.	31.391	4.380	35.771	12701.0	4.617
3000.	31.539	4.388	35.927	13163.0	4.623
3100.	31.683	4.395	36.079	13625.6	4.628
3200.	31.823	4.403	36.226	14088.6	4.633
3300.	31.959	4.410	36.368	14552.2	4.638
3400.	32.090	4.417	36.507	15016.3	4.643
3500.	32.219	4.423	36.642	15480.9	4.648
3600.	32.343	4.429	36.773	15946.0	4.653
3700.	32.465	4.436	36.900	16411.5	4.658
3800.	32.583	4.441	37.025	16877.6	4.663
3900.	32.699	4.447	37.146	17344.2	4.668
4000.	32.811	4.453	37.264	17811.3	4.673
4100.	32.921	4.458	37.379	18278.8	4.678
4200.	33.029	4.464	37.492	18746.8	4.683
4300.	33.134	4.469	37.602	19215.3	4.687
4400.	33.237	4.474	37.710	19684.3	4.692
4500.	33.337	4.479	37.816	20153.8	4.697
4600.	33.436	4.483	37.919	20623.7	4.702
4700.	33.532	4.488	38.020	21094.1	4.706
4800.	33.627	4.493	38.119	21565.0	4.711
4900.	33.719	4.497	38.217	22036.3	4.716
5000.	33.810	4.502	38.312	22508.1	4.720
5100.	33.899	4.506	38.405	22980.4	4.725
5200.	33.987	4.510	38.497	23453.1	4.730
5300.	34.073	4.514	38.587	23926.4	4.734
5400.	34.157	4.519	38.676	24400.0	4.739
5500.	34.240	4.523	38.763	24874.2	4.744
5600.	34.322	4.527	38.848	25348.8	4.748
5700.	34.402	4.530	38.932	25823.8	4.753
5800.	34.481	4.534	39.015	26299.4	4.758
5900.	34.558	4.538	39.097	26775.3	4.762
6000.	34.635	4.542	39.177	27251.8	4.767
273.15	21.964	3.566	25.531	974.2	3.783
298.15	22.278	3.587	25.865	1069.5	3.841

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal mole^{-1} °K^{-1} (or °C^{-1})	1.98726
cal g^{-1} °K^{-1} (or °C^{-1})	0.043220
joules g^{-1} °K^{-1} (or °C^{-1})	0.180833
Btu (lb mole)$^{-1}$ °R^{-1} (or °F^{-1})	1.98595
Btu lb^{-1} °R^{-1} (or °F^{-1})	0.043192

Table 11. Thermodynamic Functions for AlCl

T °K	$\frac{-(F^o-H^o_0)}{RT}$	$\frac{H^o - H^o_0}{RT}$	$\frac{S^o}{R}$	$\frac{H^o - H^o_0}{R}$	$\frac{C^o_p}{R}$
50.	17.290	3.498	20.788	174.9	3.501
75.	18.709	3.500	22.208	262.5	3.510
100.	19.716	3.507	23.223	350.7	3.551
125.	20.500	3.523	24.023	440.3	3.628
150.	21.145	3.548	24.693	532.2	3.724
175.	21.694	3.580	25.274	626.5	3.822
200.	22.174	3.616	25.790	723.2	3.913
225.	22.602	3.654	26.256	822.1	3.994
250.	22.989	3.691	26.680	922.8	4.063
275.	23.343	3.728	27.071	1025.1	4.122
300.	23.669	3.763	27.431	1128.8	4.172
325.	23.971	3.796	27.767	1233.7	4.214
350.	24.254	3.827	28.081	1339.5	4.250
375.	24.519	3.856	28.375	1446.1	4.281
400.	24.768	3.884	28.652	1553.5	4.308
425.	25.005	3.909	28.914	1661.5	4.331
450.	25.229	3.933	29.162	1770.0	4.351
475.	25.442	3.956	29.398	1879.0	4.369
500.	25.645	3.977	29.622	1988.4	4.384
550.	26.026	4.015	30.041	2208.3	4.410
600.	26.377	4.049	30.426	2429.4	4.432
650.	26.702	4.079	30.782	2651.4	4.449
700.	27.006	4.106	31.112	2874.3	4.464
750.	27.290	4.130	31.420	3097.8	4.476
800.	27.557	4.152	31.710	3321.9	4.487
850.	27.810	4.172	31.982	3546.5	4.497
900.	28.049	4.191	32.239	3771.5	4.505
950.	28.276	4.207	32.483	3997.0	4.513
1000.	28.492	4.223	32.715	4222.8	4.520
1050.	28.698	4.237	32.935	4449.0	4.527
1100.	28.896	4.250	33.146	4675.5	4.533
1150.	29.085	4.263	33.348	4902.2	4.538
1200.	29.266	4.274	33.541	5129.3	4.544
1250.	29.441	4.285	33.726	5356.6	4.549
1300.	29.609	4.296	33.905	5584.2	4.554
1350.	29.772	4.305	34.077	5812.0	4.558
1400.	29.928	4.314	34.243	6040.0	4.563
1450.	30.080	4.323	34.403	6268.2	4.567
1500.	30.227	4.331	34.558	6496.7	4.571
1550.	30.369	4.339	34.708	6725.3	4.575
1600.	30.507	4.346	34.853	6954.2	4.579
1650.	30.641	4.353	34.994	7183.2	4.583
1700.	30.771	4.360	35.131	7412.5	4.587
1750.	30.897	4.367	35.264	7641.9	4.590
1800.	31.020	4.373	35.393	7871.5	4.594
1850.	31.140	4.379	35.519	8101.3	4.598
1900.	31.257	4.385	35.642	8331.3	4.601
1950.	31.371	4.390	35.761	8561.5	4.605
2000.	31.482	4.396	35.878	8791.8	4.608
2050.	31.591	4.401	35.992	9022.3	4.612
2100.	31.697	4.406	36.103	9253.0	4.615
2150.	31.801	4.411	36.212	9483.8	4.618
2200.	31.902	4.416	36.318	9714.8	4.622
2250.	32.001	4.420	36.422	9946.0	4.625
2300.	32.099	4.425	36.524	10177.3	4.628
2350.	32.194	4.429	36.623	10408.8	4.632
2400.	32.287	4.434	36.721	10640.5	4.635

This table has been computed for the ground state of the molecule, which is taken as $^1\Sigma$, using the following molecular constants: B_e = 0.242 cm^{-1}, α_e = 0.002 cm^{-1}, D_e = 0.24 x 10^{-6} cm^{-1}, $\omega_e x_e$ = 1.95 cm^{-1}, and ω_e = 481.3 cm^{-1}. See reverse side for conversion factors.

Table 11. Thermodynamic Functions for AlCl - Continued

T °K	$\frac{-(F^o-H^o_0)}{RT}$	$\frac{H^o-H^o_0}{RT}$	$\frac{S^o}{R}$	$\frac{H^o-H^o_0}{R}$	$\frac{C^o_p}{R}$
2450.	32.379	4.438	36.816	10872.3	4.638
2500.	32.468	4.442	36.910	11104.3	4.641
2600.	32.643	4.450	37.092	11568.8	4.648
2700.	32.811	4.457	37.268	12033.9	4.654
2800.	32.973	4.464	37.437	12499.6	4.660
2900.	33.130	4.471	37.601	12965.9	4.667
3000.	33.281	4.478	37.759	13432.9	4.673
3100.	33.428	4.484	37.912	13900.5	4.679
3200.	33.571	4.490	38.061	14368.7	4.685
3300.	33.709	4.496	38.205	14837.5	4.691
3400.	33.843	4.502	38.345	15307.0	4.697
3500.	33.974	4.508	38.482	15777.0	4.704
3600.	34.101	4.513	38.614	16247.7	4.710
3700.	34.225	4.519	38.743	16719.0	4.716
3800.	34.345	4.524	38.869	17190.9	4.722
3900.	34.463	4.529	38.992	17663.3	4.728
4000.	34.578	4.534	39.112	18136.4	4.734
4100.	34.690	4.539	39.229	18610.1	4.740
4200.	34.799	4.544	39.343	19084.4	4.746
4300.	34.906	4.549	39.455	19559.3	4.752
4400.	35.011	4.553	39.564	20034.8	4.758
4500.	35.113	4.558	39.671	20510.9	4.764
4600.	35.213	4.563	39.776	20987.6	4.770
4700.	35.311	4.567	39.878	21464.9	4.776
4800.	35.408	4.571	39.979	21942.8	4.782
4900.	35.502	4.576	40.078	22421.3	4.788
5000.	35.594	4.580	40.175	22900.4	4.794
5100.	35.685	4.584	40.270	23380.1	4.800
5200.	35.774	4.589	40.363	23860.4	4.806
5300.	35.862	4.593	40.454	24341.3	4.812
5400.	35.948	4.597	40.544	24822.7	4.818
5500.	36.032	4.601	40.633	25304.8	4.824
5600.	36.115	4.605	40.720	25787.5	4.830
5700.	36.196	4.609	40.805	26270.7	4.836
5800.	36.277	4.613	40.890	26754.6	4.842
5900.	36.356	4.617	40.972	27239.1	4.848
6000.	36.433	4.621	41.054	27724.1	4.853
273.15	23.318	3.725	27.043	1017.5	4.118
298.15	23.645	3.760	27.406	1121.1	4.168

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal mole^{-1} °K^{-1} (or °C^{-1})	1.98726
cal g^{-1} °K^{-1} (or °C^{-1})	0.031828
joules g^{-1} °K^{-1} (or °C^{-1})	0.133169
Btu (lb mole)$^{-1}$ °R^{-1} (or °F^{-1})	1.98595
Btu lb^{-1} °R^{-1} (or °F^{-1})	0.031807

Table 12. Thermodynamic Functions for AlO

T °K	$\frac{-(F^{\circ}-H_0^{\circ})}{RT}$	$\frac{H^{\circ}-H_0^{\circ}}{RT}$	$\frac{S^{\circ}}{R}$	$\frac{H^{\circ}-H_0^{\circ}}{R}$	$\frac{C_p^{\circ}}{R}$
50.	16.452	3.494	19.946	174.7	3.500
75.	17.870	3.496	21.366	262.2	3.501
100.	18.876	3.497	22.373	349.7	3.501
125.	19.656	3.498	23.154	437.3	3.503
150.	20.294	3.499	23.793	524.9	3.509
175.	20.834	3.502	24.335	612.8	3.524
200.	21.301	3.506	24.807	701.2	3.549
225.	21.715	3.513	25.227	790.3	3.582
250.	22.085	3.521	25.607	880.4	3.623
275.	22.421	3.533	25.954	971.5	3.669
300.	22.729	3.546	26.276	1063.9	3.718
325.	23.014	3.561	26.575	1157.4	3.767
350.	23.278	3.578	26.856	1252.2	3.816
375.	23.526	3.595	27.121	1348.2	3.863
400.	23.758	3.613	27.372	1445.3	3.907
425.	23.978	3.632	27.610	1543.6	3.949
450.	24.186	3.651	27.837	1642.8	3.989
475.	24.384	3.669	28.053	1743.0	4.025
500.	24.573	3.688	28.261	1844.0	4.059
550.	24.926	3.725	28.650	2048.5	4.119
600.	25.251	3.760	29.011	2255.8	4.170
650.	25.554	3.793	29.347	2465.4	4.214
700.	25.836	3.824	29.660	2677.1	4.251
750.	26.101	3.854	29.955	2890.5	4.283
800.	26.350	3.882	30.232	3105.3	4.311
850.	26.587	3.908	30.494	3321.5	4.335
900.	26.811	3.932	30.743	3538.8	4.356
950.	27.024	3.955	30.979	3757.1	4.375
1000.	27.227	3.976	31.203	3976.3	4.391
1050.	27.422	3.996	31.418	4196.2	4.406
1100.	27.608	4.015	31.623	4416.8	4.419
1150.	27.787	4.033	31.820	4638.1	4.431
1200.	27.959	4.050	32.009	4860.0	4.442
1250.	28.125	4.066	32.190	5082.3	4.452
1300.	28.284	4.081	32.365	5305.2	4.461
1350.	28.439	4.095	32.534	5528.4	4.470
1400.	28.588	4.109	32.696	5752.1	4.477
1450.	28.732	4.121	32.854	5976.2	4.485
1500.	28.872	4.134	33.006	6200.6	4.491
1550.	29.008	4.145	33.153	6425.3	4.498
1600.	29.140	4.156	33.296	6650.3	4.504
1650.	29.268	4.167	33.435	6875.6	4.509
1700.	29.392	4.177	33.570	7101.2	4.515
1750.	29.514	4.187	33.700	7327.1	4.520
1800.	29.632	4.196	33.828	7553.2	4.524
1850.	29.747	4.205	33.952	7779.5	4.529
1900.	29.859	4.214	34.073	8006.1	4.533
1950.	29.969	4.222	34.191	8232.9	4.538
2000.	30.076	4.230	34.305	8459.9	4.542
2050.	30.180	4.238	34.418	8687.0	4.546
2100.	30.282	4.245	34.527	8914.4	4.549
2150.	30.382	4.252	34.634	9142.0	4.553
2200.	30.480	4.259	34.739	9369.7	4.557
2250.	30.576	4.266	34.841	9597.7	4.560
2300.	30.670	4.272	34.942	9825.8	4.564
2350.	30.762	4.278	35.040	10054.0	4.567
2400.	30.852	4.284	35.136	10282.5	4.570

This table has been computed for the ground state of the molecule, which is taken as $^2\Sigma$, using the following molecular constants: $B_e = 0.6414$ cm^{-1}, $\alpha_e = 0.00580$ cm^{-1}, $D_e = 1.08 \times 10^{-6}$ cm^{-1}, $\omega_e x_e = 6.97$ cm^{-1}, and $\omega_e = 979.23$ cm^{-1}. See reverse side for conversion factors.

Table 12. Thermodynamic Functions for AlO - Continued

T °K	$\frac{-(F^o-H^o_0)}{RT}$	$\frac{H^o-H^o_0}{RT}$	$\frac{S^o}{R}$	$\frac{H^o-H^o_0}{R}$	$\frac{C^o_p}{R}$
2450.	30.940	4.290	35.230	10511.1	4.573
2500.	31.027	4.296	35.323	10739.8	4.576
2600.	31.196	4.307	35.502	11197.8	4.583
2700.	31.358	4.317	35.675	11656.3	4.588
2800.	31.516	4.327	35.842	12115.4	4.594
2900.	31.668	4.336	36.004	12575.1	4.599
3000.	31.815	4.345	36.160	13035.3	4.605
3100.	31.957	4.354	36.311	13496.0	4.610
3200.	32.096	4.362	36.457	13957.3	4.615
3300.	32.230	4.369	36.599	14419.1	4.620
3400.	32.361	4.377	36.737	14881.4	4.625
3500.	32.488	4.384	36.872	15344.1	4.630
3600.	32.611	4.391	37.002	15807.4	4.635
3700.	32.732	4.398	37.129	16271.1	4.640
3800.	32.849	4.404	37.253	16735.3	4.644
3900.	32.963	4.410	37.374	17200.0	4.649
4000.	33.075	4.416	37.491	17665.1	4.654
4100.	33.184	4.422	37.606	18130.7	4.658
4200.	33.291	4.428	37.719	18596.8	4.663
4300.	33.395	4.433	37.828	19063.3	4.667
4400.	33.497	4.439	37.936	19530.3	4.672
4500.	33.597	4.444	38.041	19997.7	4.676
4600.	33.695	4.449	38.144	20465.5	4.681
4700.	33.790	4.454	38.244	20933.8	4.685
4800.	33.884	4.459	38.343	21402.6	4.690
4900.	33.976	4.464	38.440	21871.8	4.694
5000.	34.066	4.468	38.535	22341.4	4.698
5100.	34.155	4.473	38.628	22811.4	4.703
5200.	34.242	4.477	38.719	23281.9	4.707
5300.	34.327	4.482	38.809	23752.8	4.711
5400.	34.411	4.486	38.897	24224.2	4.716
5500.	34.493	4.490	38.983	24696.0	4.720
5600.	34.574	4.494	39.069	25168.2	4.724
5700.	34.654	4.498	39.152	25640.8	4.729
5800.	34.732	4.502	39.234	26113.9	4.733
5900.	34.809	4.506	39.315	26587.4	4.737
6000.	34.885	4.510	39.395	27061.3	4.741
273.15	22.398	3.532	25.929	964.7	3.666
298.15	22.707	3.545	26.253	1057.0	3.714

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal mole^{-1} °K^{-1} (or °C^{-1})	1.98726
cal g^{-1} °K^{-1} (or °C^{-1})	0.046237
joules g^{-1} °K^{-1} (or °C^{-1})	0.193455
Btu (lb mole)$^{-1}$ °R^{-1} (or °F^{-1})	1.98595
Btu lb^{-1} °R^{-1} (or °F^{-1})	0.046206

Table 13. Thermodynamic Functions for F_2

T °K	$\frac{-(F^o-H_0^o)}{RT}$	$\frac{H^o-H_0^o}{RT}$	$\frac{S^o}{R}$	$\frac{H^o-H_0^o}{R}$	$\frac{C_p^o}{R}$
50.	14.560	3.492	18.052	174.6	3.501
75.	15.976	3.495	19.471	262.1	3.501
100.	16.982	3.496	20.478	349.6	3.502
125.	17.762	3.498	21.260	437.2	3.505
150.	18.400	3.500	21.900	525.0	3.516
175.	18.940	3.503	22.443	613.1	3.538
200.	19.408	3.510	22.918	702.0	3.571
225.	19.822	3.519	23.341	791.7	3.614
250.	20.193	3.531	23.724	882.7	3.663
275.	20.530	3.545	24.076	974.9	3.716
300.	20.840	3.562	24.401	1068.5	3.771
325.	21.125	3.580	24.705	1163.5	3.824
350.	21.391	3.599	24.991	1259.7	3.876
375.	21.640	3.619	25.260	1357.2	3.924
400.	21.875	3.640	25.514	1455.9	3.970
425.	22.096	3.660	25.756	1555.7	4.013
450.	22.306	3.681	25.987	1656.5	4.052
475.	22.505	3.702	26.207	1758.3	4.088
500.	22.696	3.722	26.418	1860.9	4.122
550.	23.052	3.761	26.813	2068.5	4.181
600.	23.381	3.798	27.179	2278.9	4.231
650.	23.687	3.833	27.520	2491.5	4.274
700.	23.972	3.866	27.838	2706.1	4.310
750.	24.240	3.897	28.136	2922.5	4.342
800.	24.492	3.925	28.417	3140.3	4.369
850.	24.731	3.952	28.683	3359.3	4.393
900.	24.957	3.977	28.935	3579.6	4.415
950.	25.173	4.001	29.174	3800.8	4.434
1000.	25.379	4.023	29.402	4022.9	4.451
1050.	25.576	4.044	29.619	4245.9	4.467
1100.	25.764	4.063	29.827	4469.5	4.481
1150.	25.945	4.082	30.027	4693.9	4.494
1200.	26.119	4.099	30.218	4918.9	4.506
1250.	26.287	4.116	30.403	5144.5	4.517
1300.	26.449	4.131	30.580	5370.6	4.527
1350.	26.605	4.146	30.751	5597.2	4.537
1400.	26.756	4.160	30.916	5824.3	4.546
1450.	26.902	4.174	31.076	6051.8	4.555
1500.	27.044	4.187	31.230	6279.8	4.563
1550.	27.181	4.199	31.380	6508.2	4.571
1600.	27.315	4.211	31.525	6736.9	4.579
1650.	27.445	4.222	31.666	6966.1	4.586
1700.	27.571	4.233	31.804	7195.6	4.593
1750.	27.694	4.243	31.937	7425.4	4.600
1800.	27.813	4.253	32.066	7655.6	4.607
1850.	27.930	4.263	32.193	7886.1	4.613
1900.	28.044	4.272	32.316	8116.9	4.620
1950.	28.155	4.281	32.436	8348.0	4.626
2000.	28.263	4.290	32.553	8579.5	4.632
2050.	28.369	4.298	32.668	8811.2	4.637
2100.	28.473	4.306	32.779	9043.2	4.643
2150.	28.575	4.314	32.889	9275.5	4.649
2200.	28.674	4.322	32.996	9508.1	4.654
2250.	28.771	4.329	33.100	9740.9	4.660
2300.	28.866	4.337	33.203	9974.1	4.665
2350.	28.960	4.344	33.303	10207.5	4.670
2400.	29.051	4.350	33.402	10441.1	4.676

This table has been computed for the ground state of the molecule, which is taken as $^1\Sigma$, using the following molecular constants: $B_e = 0.8901$ cm^{-1}, $\alpha_e = 0.0146$ cm^{-1}, $D_e = 3.34 \times 10^{-6}$ cm^{-1}, $\omega_e x_e = 13.6$ cm^{-1}, and $\omega_e = 919.0$ cm^{-1}. See reverse side for conversion factors.

Table 13. Thermodynamic Functions for F_2 - Continued

T °K	$\frac{-(F^o-H_0^o)}{RT}$	$\frac{H^o-H_0^o}{RT}$	$\frac{S^o}{R}$	$\frac{H^o-H_0^o}{R}$	$\frac{C_p^o}{R}$
2450.	29.141	4.357	33.498	10675.0	4.681
2500.	29.229	4.364	33.593	10909.2	4.686
2600.	29.400	4.376	33.777	11378.3	4.696
2700.	29.566	4.388	33.954	11848.4	4.706
2800.	29.726	4.400	34.125	12319.5	4.716
2900.	29.880	4.411	34.291	12791.5	4.725
3000.	30.030	4.421	34.451	13264.5	4.735
3100.	30.175	4.432	34.607	13738.4	4.744
3200.	30.316	4.442	34.758	14213.3	4.753
3300.	30.453	4.451	34.904	14689.1	4.762
3400.	30.586	4.461	35.046	15165.8	4.772
3500.	30.715	4.470	35.185	15643.4	4.781
3600.	30.841	4.478	35.319	16121.9	4.790
3700.	30.964	4.487	35.451	16601.3	4.799
3800.	31.084	4.495	35.579	17081.6	4.807
3900.	31.201	4.503	35.704	17562.8	4.816
4000.	31.315	4.511	35.826	18044.8	4.825
4100.	31.426	4.519	35.945	18527.8	4.834
4200.	31.535	4.527	36.062	19011.6	4.843
4300.	31.642	4.534	36.176	19496.3	4.851
4400.	31.746	4.541	36.287	19981.9	4.860
4500.	31.848	4.549	36.397	20468.3	4.869
4600.	31.948	4.556	36.504	20955.6	4.877
4700.	32.046	4.563	36.609	21443.8	4.886
4800.	32.143	4.569	36.712	21932.8	4.895
4900.	32.237	4.576	36.813	22422.7	4.903
5000.	32.329	4.583	36.912	22913.5	4.912
5100.	32.420	4.589	37.009	23405.1	4.920
5200.	32.509	4.596	37.105	23897.5	4.929
5300.	32.597	4.602	37.199	24390.9	4.938
5400.	32.683	4.608	37.291	24885.0	4.946
5500.	32.768	4.615	37.382	25380.1	4.955
5600.	32.851	4.621	37.471	25876.0	4.963
5700.	32.933	4.627	37.559	26372.7	4.972
5800.	33.013	4.633	37.646	26870.3	4.980
5900.	33.092	4.639	37.731	27368.7	4.989
6000.	33.170	4.645	37.815	27868.0	4.997
273.15	20.507	3.544	24.051	968.1	3.712
298.15	20.818	3.560	24.378	1061.6	3.767

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal mole^{-1} °K^{-1} (or °C^{-1})	1.98726
cal g^{-1} °K^{-1} (or °C^{-1})	0.052296
joules g^{-1} °K^{-1} (or °C^{-1})	0.218808
Btu (lb mole)$^{-1}$ °R^{-1} (or °F^{-1})	1.98595
Btu lb^{-1} °R^{-1} (or °F^{-1})	0.052262

Table 14. Thermodynamic Functions for Cl_2

T °K	$\frac{-(F^o - H^o_0)}{RT}$	$\frac{H^o - H^o_0}{RT}$	$\frac{S^o}{R}$	$\frac{H^o - H^o_0}{R}$	$\frac{C^o_p}{R}$
50.	16.794	3.498	20.292	174.9	3.500
75.	18.212	3.499	21.711	262.4	3.503
100.	19.219	3.502	22.721	350.2	3.523
125.	20.001	3.511	23.512	438.8	3.571
150.	20.643	3.527	24.169	529.0	3.644
175.	21.188	3.549	24.737	621.1	3.727
200.	21.664	3.577	25.240	715.4	3.812
225.	22.087	3.607	25.694	811.7	3.893
250.	22.468	3.640	26.108	909.9	3.965
275.	22.817	3.672	26.489	1009.9	4.030
300.	23.138	3.704	26.842	1111.3	4.086
325.	23.436	3.736	27.171	1214.1	4.135
350.	23.713	3.766	27.479	1318.0	4.177
375.	23.974	3.794	27.769	1422.9	4.214
400.	24.220	3.822	28.042	1528.7	4.246
425.	24.452	3.847	28.300	1635.2	4.274
450.	24.673	3.872	28.545	1742.3	4.299
475.	24.883	3.895	28.778	1850.1	4.321
500.	25.083	3.917	29.000	1958.3	4.340
550.	25.459	3.957	29.415	2176.2	4.373
600.	25.804	3.993	29.797	2395.5	4.399
650.	26.125	4.025	30.150	2616.0	4.421
700.	26.425	4.054	30.478	2837.6	4.439
750.	26.705	4.080	30.785	3059.9	4.455
800.	26.969	4.104	31.073	3283.0	4.469
850.	27.219	4.126	31.344	3506.8	4.480
900.	27.455	4.146	31.601	3731.0	4.491
950.	27.680	4.164	31.844	3955.8	4.500
1000.	27.894	4.181	32.075	4181.1	4.509
1050.	28.098	4.197	32.295	4406.7	4.517
1100.	28.294	4.212	32.505	4632.7	4.524
1150.	28.481	4.225	32.707	4859.1	4.530
1200.	28.661	4.238	32.900	5085.7	4.537
1250.	28.835	4.250	33.085	5312.7	4.543
1300.	29.002	4.262	33.263	5540.0	4.548
1350.	29.163	4.272	33.435	5767.5	4.553
1400.	29.318	4.282	33.601	5995.3	4.558
1450.	29.469	4.292	33.761	6223.4	4.563
1500.	29.614	4.301	33.915	6451.6	4.568
1550.	29.755	4.310	34.065	6680.2	4.573
1600.	29.892	4.318	34.210	6908.9	4.577
1650.	30.025	4.326	34.351	7137.9	4.581
1700.	30.155	4.334	34.488	7367.0	4.585
1750.	30.280	4.341	34.621	7596.4	4.590
1800.	30.403	4.348	34.751	7826.0	4.594
1850.	30.522	4.354	34.876	8055.8	4.597
1900.	30.638	4.361	34.999	8285.7	4.601
1950.	30.752	4.367	35.119	8515.9	4.605
2000.	30.862	4.373	35.235	8746.2	4.609
2050.	30.970	4.379	35.349	8976.8	4.613
2100.	31.076	4.385	35.460	9207.5	4.616
2150.	31.179	4.390	35.569	9438.4	4.620
2200.	31.280	4.395	35.675	9669.5	4.623
2250.	31.379	4.400	35.779	9900.8	4.627
2300.	31.476	4.405	35.881	10132.2	4.631
2350.	31.570	4.410	35.981	10363.8	4.634
2400.	31.663	4.415	36.078	10595.6	4.637

This table has been computed for the ground state of the molecule, which is taken as $^1\Sigma$, using the following molecular constants: $B_e = 0.2404$ cm^{-1}, $\alpha_e = 0.00166$ cm^{-1}, $D_e = 0.1766 \times 10^{-6}$ cm^{-1}, $\omega_e x_e = 3.94$ cm^{-1}, and $\omega_e = 561.0$ cm^{-1}. See reverse side for conversion factors.

Table 14. Thermodynamic Functions for Cl_2 - Continued

T °K	$\frac{-(F^\circ - H_0^\circ)}{RT}$	$\frac{H^\circ - H_0^\circ}{RT}$	$\frac{S^\circ}{R}$	$\frac{H^\circ - H_0^\circ}{R}$	$\frac{C_p^\circ}{R}$
2450.	31.754	4.419	36.174	10827.6	4.641
2500.	31.844	4.424	36.268	11059.7	4.644
2600.	32.017	4.432	36.450	11524.5	4.651
2700.	32.185	4.441	36.626	11989.9	4.658
2800.	32.347	4.449	36.795	12456.0	4.664
2900.	32.503	4.456	36.959	12922.8	4.671
3000.	32.654	4.463	37.117	13390.2	4.678
3100.	32.800	4.470	37.271	13858.3	4.684
3200.	32.942	4.477	37.420	14327.0	4.690
3300.	33.080	4.484	37.564	14796.4	4.697
3400.	33.214	4.490	37.704	15266.4	4.703
3500.	33.345	4.496	37.841	15737.0	4.710
3600.	33.471	4.502	37.974	16208.3	4.716
3700.	33.595	4.508	38.103	16680.3	4.722
3800.	33.715	4.514	38.229	17152.8	4.729
3900.	33.832	4.519	38.352	17626.0	4.735
4000.	33.947	4.525	38.472	18099.8	4.741
4100.	34.059	4.530	38.589	18574.3	4.748
4200.	34.168	4.536	38.703	19049.3	4.754
4300.	34.275	4.541	38.815	19525.0	4.760
4400.	34.379	4.546	38.925	20001.4	4.766
4500.	34.481	4.551	39.032	20478.3	4.773
4600.	34.581	4.556	39.137	20955.9	4.779
4700.	34.679	4.560	39.240	21434.1	4.785
4800.	34.775	4.565	39.341	21912.9	4.791
4900.	34.870	4.570	39.440	22392.4	4.798
5000.	34.962	4.574	39.537	22872.4	4.804
5100.	35.053	4.579	39.632	23353.1	4.810
5200.	35.142	4.584	39.725	23834.4	4.816
5300.	35.229	4.588	39.817	24316.3	4.822
5400.	35.315	4.592	39.907	24798.9	4.828
5500.	35.399	4.597	39.996	25282.0	4.835
5600.	35.482	4.601	40.083	25765.8	4.841
5700.	35.563	4.605	40.169	26250.2	4.847
5800.	35.644	4.610	40.253	26735.2	4.853
5900.	35.722	4.614	40.336	27220.8	4.859
6000.	35.800	4.618	40.418	27707.1	4.866
273.15	22.792	3.670	26.462	1002.4	4.025
298.15	23.115	3.702	26.817	1103.8	4.082

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal $mole^{-1}$ $°K^{-1}$ (or $°C^{-1}$)	1.98726
cal g^{-1} $°K^{-1}$ (or $°C^{-1}$)	0.028024
joules g^{-1} $°K^{-1}$ (or $°C^{-1}$)	0.117250
Btu $(lb\ mole)^{-1}$ $°R^{-1}$ (or $°F^{-1}$)	1.98595
Btu lb^{-1} $°R^{-1}$ (or $°F^{-1}$)	0.028005

Table 15. Thermodynamic Functions for ClF

T °K	$\frac{-(F^{\circ}-H_0^{\circ})}{RT}$	$\frac{H^{\circ}-H_0^{\circ}}{RT}$	$\frac{S^{\circ}}{R}$	$\frac{H^{\circ}-H_0^{\circ}}{R}$	$\frac{C_p^{\circ}}{R}$
50.	16.334	3.495	19.829	174.8	3.500
75.	17.752	3.497	21.249	262.3	3.501
100.	18.758	3.498	22.256	349.8	3.503
125.	19.539	3.500	23.039	437.5	3.512
150.	20.177	3.504	23.681	525.5	3.535
175.	20.718	3.511	24.228	614.4	3.573
200.	21.187	3.521	24.709	704.3	3.623
225.	21.603	3.536	25.139	795.6	3.681
250.	21.976	3.554	25.530	888.4	3.743
275.	22.316	3.574	25.889	982.7	3.804
300.	22.628	3.595	26.223	1078.6	3.863
325.	22.916	3.618	26.534	1175.8	3.918
350.	23.185	3.641	26.826	1274.4	3.970
375.	23.437	3.665	27.102	1374.3	4.017
400.	23.674	3.688	27.363	1475.2	4.059
425.	23.899	3.711	27.610	1577.2	4.098
450.	24.112	3.734	27.845	1680.1	4.133
475.	24.314	3.755	28.069	1783.8	4.165
500.	24.507	3.777	28.284	1888.3	4.193
550.	24.869	3.817	28.686	2099.3	4.243
600.	25.203	3.854	29.057	2312.5	4.284
650.	25.513	3.889	29.401	2527.5	4.318
700.	25.802	3.920	29.722	2744.2	4.347
750.	26.073	3.950	30.023	2962.1	4.371
800.	26.329	3.977	30.306	3181.3	4.392
850.	26.571	4.002	30.573	3401.3	4.411
900.	26.800	4.025	30.825	3622.3	4.427
950.	27.019	4.046	31.065	3844.0	4.441
1000.	27.227	4.066	31.293	4066.3	4.454
1050.	27.426	4.085	31.511	4289.3	4.465
1100.	27.616	4.103	31.719	4512.8	4.475
1150.	27.799	4.119	31.918	4736.8	4.484
1200.	27.974	4.134	32.109	4961.3	4.493
1250.	28.143	4.149	32.292	5186.1	4.501
1300.	28.306	4.163	32.469	5411.3	4.508
1350.	28.464	4.176	32.639	5636.9	4.515
1400.	28.616	4.188	32.804	5862.9	4.522
1450.	28.763	4.199	32.962	6089.1	4.528
1500.	28.906	4.210	33.116	6315.6	4.533
1550.	29.044	4.221	33.265	6542.4	4.539
1600.	29.178	4.231	33.409	6769.5	4.544
1650.	29.308	4.241	33.549	6996.9	4.549
1700.	29.435	4.250	33.685	7224.4	4.554
1750.	29.558	4.258	33.817	7452.2	4.559
1800.	29.678	4.267	33.945	7680.3	4.563
1850.	29.795	4.275	34.070	7908.5	4.567
1900.	29.910	4.283	34.192	8137.0	4.572
1950.	30.021	4.290	34.311	8365.7	4.576
2000.	30.130	4.297	34.427	8594.6	4.580
2050.	30.236	4.304	34.540	8823.6	4.583
2100.	30.340	4.311	34.651	9052.9	4.587
2150.	30.441	4.317	34.758	9282.4	4.591
2200.	30.540	4.324	34.864	9512.0	4.595
2250.	30.638	4.330	34.967	9741.8	4.598
2300.	30.733	4.336	35.068	9971.8	4.602
2350.	30.826	4.341	35.167	10202.0	4.605
2400.	30.918	4.347	35.264	10432.3	4.609

This table has been computed for the ground state of the molecule, which is taken as $^1\Sigma$, using the following molecular constants: $B_e = 0.514012\ \mathrm{cm}^{-1}$, $\alpha_e = 0.0043272\ \mathrm{cm}^{-1}$, $D_e = 0.869 \times 10^{-6}\ \mathrm{cm}^{-1}$, $\omega_e x_e = 6.20\ \mathrm{cm}^{-1}$, and $\omega_e = 784.43\ \mathrm{cm}^{-1}$. See reverse side for conversion factors.

Table 15. Thermodynamic Functions for ClF - Continued

T °K	$\frac{-(F^\circ - H^\circ_0)}{RT}$	$\frac{H^\circ - H^\circ_0}{RT}$	$\frac{S^\circ}{R}$	$\frac{H^\circ - H^\circ_0}{R}$	$\frac{C^\circ_p}{R}$
2450.	31.007	4.352	35.360	10662.8	4.612
2500.	31.095	4.357	35.453	10893.5	4.615
2600.	31.266	4.367	35.634	11355.4	4.622
2700.	31.431	4.377	35.808	11817.9	4.628
2800.	31.591	4.386	35.977	12281.0	4.634
2900.	31.745	4.395	36.140	12744.8	4.641
3000.	31.894	4.403	36.297	13209.1	4.647
3100.	32.038	4.411	36.449	13674.1	4.653
3200.	32.179	4.419	36.597	14139.7	4.659
3300.	32.315	4.426	36.741	14605.8	4.665
3400.	32.447	4.433	36.880	15072.6	4.670
3500.	32.576	4.440	37.016	15539.9	4.676
3600.	32.701	4.447	37.147	16007.8	4.682
3700.	32.823	4.453	37.276	16476.3	4.688
3800.	32.941	4.459	37.401	16945.4	4.693
3900.	33.057	4.465	37.523	17415.0	4.699
4000.	33.171	4.471	37.642	17885.2	4.705
4100.	33.281	4.477	37.758	18355.9	4.710
4200.	33.389	4.483	37.872	18827.2	4.716
4300.	33.495	4.488	37.983	19299.0	4.721
4400.	33.598	4.494	38.091	19771.5	4.727
4500.	33.699	4.499	38.198	20244.4	4.732
4600.	33.798	4.504	38.302	20717.9	4.738
4700.	33.895	4.509	38.404	21192.0	4.743
4800.	33.990	4.514	38.503	21666.6	4.749
4900.	34.083	4.519	38.601	22141.8	4.754
5000.	34.174	4.523	38.698	22617.5	4.760
5100.	34.264	4.528	38.792	23093.7	4.765
5200.	34.352	4.533	38.884	23570.5	4.771
5300.	34.438	4.537	38.975	24047.9	4.776
5400.	34.523	4.542	39.065	24525.7	4.782
5500.	34.606	4.546	39.153	25004.2	4.787
5600.	34.688	4.551	39.239	25483.1	4.792
5700.	34.769	4.555	39.324	25962.6	4.798
5800.	34.848	4.559	39.407	26442.7	4.803
5900.	34.926	4.563	39.489	26923.3	4.808
6000.	35.003	4.567	39.570	27404.4	4.814
273.15	22.292	3.572	25.864	975.7	3.799
298.15	22.605	3.594	26.199	1071.4	3.859

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal mole^{-1} °K^{-1} (or °C^{-1})	1.98726
cal g^{-1} °K^{-1} (or °C^{-1})	0.036492
joules g^{-1} °K^{-1} (or °C^{-1})	0.152684
Btu (lb mole)$^{-1}$ °R^{-1} (or °F^{-1})	1.98595
Btu lb^{-1} °R^{-1} (or °F^{-1})	0.036468

Table 16. Thermodynamic Functions for ClO

T °K	$\frac{-(F^\circ - H_0^\circ)}{RT}$	$\frac{H^\circ - H_0^\circ}{RT}$	$\frac{S^\circ}{R}$	$\frac{H^\circ - H_0^\circ}{R}$	$\frac{C_p^\circ}{R}$
50.	16.716	3.494	20.211	174.7	3.501
75.	18.134	3.496	21.630	262.2	3.501
100.	19.140	3.498	22.637	349.8	3.502
125.	19.920	3.499	23.419	437.4	3.507
150.	20.558	3.501	24.060	525.2	3.521
175.	21.098	3.506	24.604	613.5	3.547
200.	21.567	3.513	25.080	702.7	3.586
225.	21.981	3.524	25.505	792.9	3.633
250.	22.353	3.538	25.891	884.4	3.687
275.	22.691	3.554	26.245	977.2	3.742
300.	23.001	3.572	26.573	1071.5	3.798
325.	23.288	3.591	26.879	1167.1	3.852
350.	23.555	3.612	27.167	1264.1	3.904
375.	23.805	3.633	27.438	1362.3	3.952
400.	24.040	3.654	27.694	1461.7	3.997
425.	24.262	3.676	27.938	1562.1	4.038
450.	24.473	3.697	28.170	1663.6	4.076
475.	24.673	3.718	28.391	1765.9	4.110
500.	24.864	3.738	28.602	1869.0	4.142
550.	25.223	3.777	29.000	2077.6	4.197
600.	25.553	3.814	29.367	2288.6	4.244
650.	25.859	3.849	29.708	2501.8	4.283
700.	26.146	3.881	30.027	2716.8	4.316
750.	26.415	3.911	30.326	2933.3	4.344
800.	26.668	3.939	30.607	3151.2	4.369
850.	26.908	3.965	30.873	3370.2	4.390
900.	27.135	3.989	31.124	3590.2	4.409
950.	27.351	4.012	31.363	3811.0	4.426
1000.	27.558	4.033	31.590	4032.7	4.441
1050.	27.755	4.052	31.807	4255.1	4.454
1100.	27.944	4.071	32.015	4478.1	4.466
1150.	28.125	4.088	32.214	4701.7	4.477
1200.	28.299	4.105	32.404	4925.8	4.487
1250.	28.467	4.120	32.588	5150.4	4.497
1300.	28.629	4.135	32.764	5375.5	4.506
1350.	28.786	4.149	32.934	5601.0	4.514
1400.	28.937	4.162	33.099	5826.8	4.521
1450.	29.083	4.175	33.257	6053.1	4.528
1500.	29.225	4.186	33.411	6279.7	4.535
1550.	29.362	4.198	33.560	6506.6	4.542
1600.	29.496	4.209	33.704	6733.8	4.548
1650.	29.625	4.219	33.844	6961.4	4.554
1700.	29.751	4.229	33.980	7189.2	4.559
1750.	29.874	4.238	34.113	7417.3	4.565
1800.	29.994	4.248	34.241	7645.7	4.570
1850.	30.110	4.256	34.366	7874.3	4.575
1900.	30.224	4.265	34.489	8103.2	4.580
1950.	30.335	4.273	34.608	8332.3	4.585
2000.	30.443	4.281	34.724	8561.6	4.589
2050.	30.549	4.288	34.837	8791.2	4.594
2100.	30.652	4.296	34.948	9021.0	4.598
2150.	30.753	4.303	35.056	9251.1	4.603
2200.	30.852	4.310	35.162	9481.3	4.607
2250.	30.949	4.316	35.266	9711.7	4.611
2300.	31.044	4.323	35.367	9942.4	4.615
2350.	31.137	4.329	35.466	10173.3	4.619
2400.	31.228	4.335	35.563	10404.3	4.623

This table has been computed for the ground state of the molecule, which is taken as $^2\Pi$, using the following molecular constants: $B_e = 0.646$ cm^{-1}, $\alpha_e = 0.007$ cm^{-1}, $D_e = 2.2 \times 10^{-6}$ cm^{-1}, $\omega_e x_e = 7.5$ cm^{-1}, and $\omega_e = 868.0$ cm^{-1}. See reverse side for conversion factors.

Table 16. Thermodynamic Functions for ClO - Continued

T °K	$\frac{-(F^{o}-H^{o}_{0})}{RT}$	$\frac{H^{o}-H^{o}_{0}}{RT}$	$\frac{S^{o}}{R}$	$\frac{H^{o}-H^{o}_{0}}{R}$	$\frac{C^{o}_{p}}{R}$
2450.	31.318	4.341	35.659	10635.6	4.627
2500.	31.406	4.347	35.752	10867.0	4.631
2600.	31.576	4.358	35.934	11330.5	4.638
2700.	31.741	4.368	36.109	11794.7	4.646
2800.	31.900	4.378	36.278	12259.7	4.653
2900.	32.054	4.388	36.442	12725.3	4.660
3000.	32.203	4.397	36.600	13191.7	4.667
3100.	32.347	4.406	36.753	13658.8	4.674
3200.	32.487	4.415	36.902	14126.6	4.681
3300.	32.623	4.423	37.046	14595.1	4.688
3400.	32.755	4.431	37.186	15064.2	4.695
3500.	32.884	4.438	37.322	15534.0	4.701
3600.	33.009	4.446	37.455	16004.5	4.708
3700.	33.131	4.453	37.584	16475.6	4.715
3800.	33.250	4.460	37.709	16947.4	4.721
3900.	33.366	4.467	37.832	17419.9	4.728
4000.	33.479	4.473	37.952	17892.9	4.734
4100.	33.589	4.480	38.069	18366.7	4.741
4200.	33.697	4.486	38.183	18841.1	4.747
4300.	33.803	4.492	38.295	19316.1	4.753
4400.	33.906	4.498	38.404	19791.7	4.760
4500.	34.007	4.504	38.511	20268.0	4.766
4600.	34.106	4.510	38.616	20745.0	4.772
4700.	34.204	4.515	38.719	21222.5	4.779
4800.	34.299	4.521	38.820	21700.7	4.785
4900.	34.392	4.526	38.918	22179.5	4.791
5000.	34.483	4.532	39.015	22659.0	4.798
5100.	34.573	4.537	39.110	23139.1	4.804
5200.	34.661	4.542	39.204	23619.8	4.810
5300.	34.748	4.547	39.295	24101.1	4.816
5400.	34.833	4.552	39.385	24583.0	4.823
5500.	34.917	4.557	39.474	25065.6	4.829
5600.	34.999	4.562	39.561	25548.8	4.835
5700.	35.080	4.567	39.647	26032.6	4.841
5800.	35.159	4.572	39.731	26517.0	4.847
5900.	35.237	4.577	39.814	27002.1	4.854
6000.	35.314	4.581	39.895	27487.7	4.860
273.15	22.667	3.552	26.220	970.3	3.738
298.15	22.979	3.570	26.549	1064.5	3.794

CONVERSION FACTORS

To Convert Tabulated Values to Quantities Having the Dimensions Indicated Below	Multiply By
cal mole^{-1} °K^{-1} (or °C^{-1})	1.98726
cal g^{-1} °K^{-1} (or °C^{-1})	0.038620
joules g^{-1} °K^{-1} (or °C^{-1})	0.161585
Btu (lb mole)$^{-1}$ °R^{-1} (or °F^{-1})	1.98595
Btu lb^{-1} °R^{-1} (or °F^{-1})	0.038594

APPENDIX I

INDEX OF THERMAL FUNCTIONS*

No.	ELEMENT	SYM.	+ IONS —	X X_n	XO X_nO	XO_2 X_nO_m	XF X_nF_m	XH X_nH_m	XN X_nN_m	XB X_nB_m	XC X_nC_m
89	Actinium	Ac		1							
13	Aluminum	Al		1, 2, 3, 4, 12, 28, 46, 47	12, 43, 46, 47		47	41, 43, 46, 47	28		
						4, 12, 46, 47					
51	Antimony	Sb		1, 2, 3, 28							
				28							
18	Argon	A	22	1, 2, 3, 4, 5, 10, 12, 21, 22, 28, 46, 47							
33	Arsenic	As		1, 2, 3, 28							
				28			28	28			
85	Astatine	At		1							
56	Barium	Ba		1, 2, 3				41			
							28				
4	Beryllium	Be		1, 2, 3, 14, 47	28, 33, 47		33, 47	41, 47			
				28					28		
83	Bismuth	Bi		1, 28, 44				41			
				28	28						
5	Boron	B		1, 2, 3, 12, 28, 33, 34, 46, 47	4, 12, 33, 34, 46, 47		4, 33, 34, 43, 46, 47	4, 33, 34, 41, 43, 46, 47	4, 28, 33, 34, 46, 47		
				10, 33, 34, 46, 47	33	4, 12, 28, 33, 34, 46, 47	4, 33, 34, 46, 47	4, 34			4, 28, 34
35	Bromine	Br		1, 2, 3, 4, 8, 14, 45				4, 28, 33, 41, 45, 47		4, 34	
				4, 8, 14, 28, 33, 45, 47			28			4, 28, 34	26, 28
48	Cadmium	Cd		1, 2, 3, 28, 44				41			
20	Calcium	Ca		1, 2, 3, 4, 14, 28	4			41			
							28		28		
6	Carbon	C	22	1, 2, 3, 4, 9, 12, 19, 20, 21, 22, 25, 28, 33, 45, 46, 47	5, 9, 12, 19, 20, 21, 25, 28, 33, 45, 46, 47	4, 5, 9, 10, 12, 19, 20, 21, 25, 28, 33, 45, 46, 47	33, 46, 47	25, 33, 41, 43, 46, 47	28, 33, 47		
				33, 46, 47			26, 28, 33, 46, 47	25, 28, 33, 45, 47	25, 28, 3346, 47	34	
58	Cerium	Ce		1, 28							
55	Cesium	Cs		1, 2, 3, 4, 7, 28, 46				41			
				7, 28							
17	Chlorine	Cl		1, 2, 3, 4, 8, 12, 14, 25, 33, 45, 46, 47	12, 33, 47	46	4, 8, 33, 43, 46, 47	4, 28, 33, 41, 45, 46, 47		4, 34, 46	
				4, 8, 12, 14, 25, 28, 33, 45, 46, 47	4, 8, 28, 46	4, 8	4, 8			4, 28, 34	26, 28
24	Chromium	Cr		1, 2, 3, 28, 44							
					28						28
27	Cobalt	Co		1, 2, 3							
29	Copper	Cu		1, 2, 3, 4, 28, 44	28			41			

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*The numbers refer to references in Appendix, pp. 6 et seq.

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No.	ELEMENT	SYM.	+ IONS −	X X_n	XO X_nO	XO_2 X_nO_m	XF X_nF_m	XH X_nH_m	XN X_nN_m	.XB X_nB_m	XC X_nC_m
66	Dysprosium	Dy		1							
68	Erbium	Er		1							
63	Europium	Eu		1							
9	Fluorine	F	12 46, 47	1, 2, 3, 4, 8, 14, 33, 45, 46, 47 4, 8, 14, 33, 46, 47	4, 8, 46		4, 8	4, 28, 33, 41, 45, 46, 47		4, 34 4, 34	33, 46 26
87	Francium	Fr		1							
64	Gadolinium	Gd		1							
31	Gallium	Ga		1, 2, 3, 28							
32	Germanium	Ge		1, 2, 3, 4							
79	Gold	Au		1, 2, 3, 28, 44				41			
72	Hafnium	Hf		1							
2	Helium	He		1, 2, 3, 4, 47							
67	Holmium	Ho		1							
1	Hydrogen	H	22	1,2,3,4,5,13,18,21, 22,25,33,45,46,47 4,5,9,10,12,13,19, 20,25,33,42,45,46,47	4,12,17,19,20,21,25, 33,42,45,46,47 4,5,9,10,12,16,19,20, 21,25,33,42,45,46,47	25	4, 28, 45, 46, 47	33	33 25, 28	34	46, 47 28, 45
49	Indium	In		21, 28, 33, 44 1, 28				41			
53	Iodine	I		1, 2, 3, 4, 8, 14 4, 8, 14, 28			4, 8 4, 8	4, 28, 41			
77	Iridium	Ir		1, 28		28					
26	Iron	Fe		1, 2, 3, 28, 44	28	28					28
36	Krypton	Kr		1, 2, 3, 4, 28							
57	Lanthanum	La		1, 2, 3, 28							
82	Lead	Pb		1, 28, 44 28	28			41			
3	Lithium	Li	12, 46, 47	1,2,3,4,7,14,28,46,47 4,7,14,28,33,46,47	47 47		47	28, 41, 46, 47	28		

*The numbers refer to references in Appendix, pp. 6 et seq.

No.	ELEMENT	SYM.	+ IONS −	X X_n	XO X_nO	XO_2 X_nO_m	XF X_nF_m	XH X_nH_m	XN X_nN_m	XB X_nB_m	XC X_nC_m
71	Lutetium	Lu		1							
12	Magnesium	Mg		1, 2, 3, 14, 28, 44, 46, 47	28, 46		46, 47 28	41, 46, 47	28		
25	Manganese	Mn		1, 2, 3, 28, 44	28	28			28		28
80	Mercury	Hg		1, 2, 3, 28 28							
42	Molybdenum	Mo		1, 44							
60	Neodymium	Nd		1							
10	Neon	Ne		1, 2, 3, 4, 47							
28	Nickel	Ni		1, 2, 3, 4, 28, 44							
41	Niobium	Nb		1, 2, 3							
7	Nitrogen	N	22 15	1,2,3,4,5,12,21,33,45, 46,47 4,5,9,10,11,12,15,19, 20,21,25,28,33,45,46,47	4,9,12,15,15^+,19,20, 21,25,28,33,45,46,47 25,28,47	25,28,33,46,47 4,28,33,47	43	33,41,46,47 4,25,28,33,47		34	46
76	Osmium	OS		1,28		28					
8	Oxygen	O	22 22 15	1,2,3,4,5,12,22,33,46, 47 4,5,10,11,12,15,19, 20,25,28,33,46,47				28,41,46,47 47	46,47 47		46
46	Palladium	Pd		1,2,3,28						28	
15	Phosphorus	P		1,2,3,28,33,46 28,33,46	33		28,33	33,41 28,33	28,33		33
78	Platinum	Pt		1,2,3,28,44							
84	Polonium	Po		1							
19	Potassium	K		1,2,3,4,7,14,28,46 4,7,14,28,46			28,46	28,41,46			
59	Praseodymium	Pr		1							
61	Promethium	Pm		1							
91	Protactinium	Pa		1							
88	Radium	Ra		1							

*The numbers refer to references in Appendix, pp. 6 et seq.

No.	ELEMENT	SYM.	+ IONS −	X X_n	XO X_nO	XO_2 X_nO_m	XF X_nF_m	XH X_nH_m	XN X_nN_m	XB X_nB_m	XC X_nC_m
86	Radon	Rn		1,4,28							
75	Rhenium	Re		1,28							
45	Rhodium	Rh		1,2,3,28							
37	Rubidium	Rb		1,2,3,4,7,28 4,6,7,28				41			
44	Ruthenium	Ru		1,28							
62	Samarium	Sm		1							
21	Scandium	Sc		1,2,3							
34	Selenium	Se		1,2,3,28 28	28		28	28			
14	Silicon	Si		1,2,3,4,28,47	47	28	28	41 28	28		28
47	Silver	Ag		1,2,3,28,44				41			
11	Sodium	Na		1,2,3,4,6,7,14,28 4,6,7,14,28	28		28	28,41			
38	Strontium	Sr		1,2,3	28			41			
16	Sulfur	S		1,2,3,4,6,27,28,33,46 4,6,27,28,33,46	4,6,27,28,33,46	4,6,25,27,28,33,46 4,6,25,28,33		18,33,41,42,46 25,27,28,33,46		34	28,33,43,46 25,28,33
73	Tantalum	Ta		1,28					28		
43	Technetium	Tc		1							
52	Tellurium	Te		1,28 28	28		28				
65	Terbium	Tb		1							
81	Thallium	Tl		1,28			28	41			
90	Thorium	Th		1,28		28			28		
69	Thulium	Tm		1							
50	Tin	Sn		1,4,28,44	28	28		41			

*The numbers refer to references in Appendix, pp. 6 et seq.

No.	ELEMENT	SYM.	+ IONS −	X X_n	XO X_nO	XO_2 X_nO_m	XF X_nF_m	XH X_nH_m	XN X_nN_m	XB X_nB_m	XC X_nC_m
22	Titanium	Ti		1, 2, 3, 4, 14, 28, 44	4, 14, 28	4, 14, 28 4, 14, 28			28		28
74	Tungsten	W		1, 28							
92	Uranium	U		1, 28		28 28					
23	Vanadium	V		1, 2, 3, 4, 28		4, 28			28		28
54	Xenon	Xe		1, 2, 3, 4, 28							
70	Ytterbium	Yb		1,							
39	Yttrium	Y		1, 2, 3							
30	Zinc	Zn		1, 2, 3, 28, 44	28	28		41			
40	Zirconium	Zr		1, 2, 3, 28, 44					28		
96	Curium	Cm									
93	Neptunium	Np									
94	Plutonium	Pu									
	Electron	e^-	46, 47								

*The numbers refer to references in Appendix, pp. 6 et seq.

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APPENDIX II

HEAT OF FUSION OF ALUMINUM OXIDE

The heat of fusion, ΔH_f, was calculated from curves of $\ln$ N vs. 1/T, where N is the mole fraction of the desired constituent and T is in degrees Kelvin. The data for these curves was obtained from available phase diagrams of aluminum oxide plus the oxides listed below. Many alumina systems were not suitable, principally, if no pure Al_2O_3 crystallized out. In cases where the data of $\ln$ vs. 1/T deviated from a straight line, the best curve was employed.

The systems identified with (*) in the table below gave data which indicated non-ideal systems. For Al_2O_3 - TiO_2, using the 1952 data [1], a ΔH_f of 45.00 kcal/mole was obtained if the curve included the given melting point of 2015° C; the best straight line gave 34.70 kcal/mole and an extrapolated melting point of 2037° C. On the basis of the systems that showed most ideal behavior, the heat of fusion of alumina should be between 23.0 and 27.0 kcal/mole. However, from these systems the melting point of alumina is still uncertain since this value is an extrapolated point on the curves. An accurate value of the alumina melting point is still desired.

The system ** indicated that impure Al_2O_3 is the likely constituent that crystallizes out.

Calculated Values for the Heat of Fusion of Al_2O_3

t_m °C	ΔH_f, Kcal/mole	System	Reference
2015°	45.00 - 34.70	*Al_2O_3 - T_iO_2	[1]
2015°	17.65	*Al_2O_3 - BeO	[2]
2042°	8.60	**Al_2O_3 - BaO	[3]
2047°	27.20	Al_2O_3 - S_iO_2	[4]
2050°	25.35	Al_2O_3 - FeO	[5]
2050°	23.55	Al_2O_3 - MnO	[6]
2030°	10.25	*Al_2O_3 - $Ca_3(PO_4)_3$	[7]
2050°	26.20	Al_2O_3 - T_iO_2	[8]
2050°	33.80	Al_2O_3 - Cr_2O_3	[9]
	24.90	Al_2O_3 - Al_4C_3	[10]

[1] Lang, S.M., Fillmore, C. L., Maxwell, L. H., J. Research Natl. Bureau Stds. 48, 301 (1952).

[2] Lang - Fillmore - Maxwell, ibid.

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[9] Bunting, ibid., 6, 947 (1931).

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